STUDY OF HOUSTON ATMOSPHERIC RADICAL PRECURSORS (SHARP) DATA ANALYSIS

AQRP Project 10-032

Final Report

Submitted to

University of Texas - Austin
Air Quality Research Program (AQRP)

By:

BARRY LEFER
University of Houston
Department of Earth and Atmospheric Sciences
Houston, TX

JOCHEN STUTZ
University of California – Los Angeles
Department of Atmospheric and Oceanic Sciences
Los Angeles, CA

XINRONG REN
University of Miami
Rosenstiel School of Marine and Atmospheric Sciences
Miami, FL

WILLIAM BRUNE
The Pennsylvania State University
Department of Meteorology
University Park, PA

JACK DIBB
University of New Hampshire
Institute for the Study of Earth, Oceans, and Space
Durham, NH

November 30, 2011
EXECUTIVE SUMMARY

During the Study of Houston Atmospheric Radical Precursors (SHARP) in spring 2009, a relatively complete suite of measurements, including OH and HO₂ mixing ratios, ozone production rates, and other ozone precursors, were performed. This provides us a unique opportunity to examine and improve the understanding of atmospheric oxidation and ozone and fine particle formation processes. The analysis of SHARP data will strengthen the understanding of atmospheric oxidation and air quality and development of the SIP, which is essential to meet the new primary and secondary National Ambient Air Quality Standards for ozone.

One way of evaluating our understanding of photochemistry and confidence in using photochemical models to inform policy is to examine how photochemical box models replicate the measured OH and HO₂ levels. In general, the models reproduced the observed OH and HO₂ with all 5 chemical mechanisms (RACM2, CB05, LaRC, SAPRC07, and MCMv3.1) producing similar levels of OH and HO₂. The differences among the 5 mechanisms are mainly due to the different treatments of VOCs. This is an encouraging result suggesting that not much modeling skill has been lost by employing lumped VOC reaction schemes in the regional chemical transport models used for SIP evaluations.

This evaluation of the OH reactivity indicates that organic intermediates did not contribute significantly to the OH reactivity in the Spring of 2009 when VOC levels (and VOC reactivity) were lower than observed in the Fall 2006 TRAMP campaign when significant unmeasured OH reactivity was observed. During SHARP, Nighttime HO₃ production from O₃+alkene reactions contributed about 68% of the total, with the remainder coming from NO₃ radical chemistry. Measurements made by long path DOAS during SHARP indicate that there is significant NO₃ formation at higher altitudes where lower nighttime NO levels are observed. The measured OH concentrations in Houston during SHARP are comparable to the OH measurements in other cities (Mexico City, Nashville, New York). The similarity of OH levels in these cities indicates that the OH production and loss rate are well buffered in urban environments.

Overall, the impact of clouds and aerosols was to reduce the net O₃ production during the SHARP campaign by an average of ~33% (~2.9 out of 8.9 ppbv/hour), compared to ~8 ppbv/hr during TRAMP. The calculated O₃ destruction rates varied in importance throughout the day, with losses due to NO₃+OH dominating the mornings indicating an excess of NOₓ which coinciding with the morning rush hour. The peak in the median diurnal net O₃ production profile was ~16 ppbv/hr which occurred around solar noon, in contrast the same analysis for the Fall 2006 TRAMP campaign found a peak net O₃ production of ~30 ppbv/hr around 11:00 AM. The Measurement of Ozone Production Sensor, MOPS, deployed during SHARP monitored in real time the rate of photochemical production of ozone, P(O₃), in ambient air. Measured and calculated P(O₃) had similar peak values but the calculated P(O₃) tended to peak earlier in the morning when NO values were higher. Measured and modeled P(O₃) had a similar dependence on NO, but the modeled P(O₃) was only half the measured P(O₃). This difference indicates possible missing radical sources in the box model with the RACM2 mechanism and thus has implications for the ability of air quality models to accurately predict ozone production rates.

The ozone production sensitivity to NOₓ or VOCs in Houston had a similar behavior for the following three campaigns: TexAQS 2000 (late summer), TRAMP 2006 (fall) and SHARP 2009 (spring); where it was VOC sensitive in the early morning and late afternoon but NOₓ sensitive throughout the afternoon. The afternoon ozone sensitivity in SHARP 2009 has a longer NOₓ-sensitive period than TexAQS 2000 and TRAMP 2006, indicating that NOₓ control is an efficient approach for the O₃ control in spring time.
During SHARP, the calculated HO₅ production was dominated by photolysis of HONO in the early morning and by O₃ photolysis in the midday. On average, the daily HO₅ production rate was 23.8 ppbv day⁻¹, of which 31% is from O₃ photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O₃ reactions with alkenes. For HO₅ loss, the clearly dominant process was the OH reaction with NO₂. Steady-state HONO mixing ratios were about 0.02 ppb in the late morning and decreased to 0.01 ppb in the afternoon. This analysis concluded that the most likely new source of daytime HONO is the photocatalytic conversion of NO₂ on ground surfaces. The slope between this HONO production source and solar irradiance are quite similar on all days, allowing for the calculation of the following general parameterization of HONO formation in the lower 300m of the Houston atmosphere: \( P_{\text{HONO}} = 3.3 \times 10^{-8} \text{m}^2\text{W}^{-1}\text{s}^{-1} \times (\text{visible solar irradiance}) \times [\text{NO}_2] \).

The evaluation of role of ClNO₂ as an early morning source of radicals and its contribution to O₃ production found that without additional chlorine sources in the model, the modeled organic peroxy radicals initiated by Cl is less than 1% of those initiated by OH and O₃. The modeled concentrations of Cl and Cl₂ are too low compared to previous observations, indicating that additional chlorine sources are needed in the model in order for the Cl chemistry to be important in photochemistry and ozone production. This analysis indicates additional measurements of chlorine species are needed to assess the potential role of halogen chemistry in the Houston atmosphere. Correlations between gaseous HNO₃ and gas phase chloride were highly correlated on short (minutes to hours) time scales throughout the SHARP campaign. Similar observations made during TexAQS 2006 on the Moody Tower and the NOAA vessel Ronald H. Brown indicate that abundant soluble Cl⁻, linked with HNO₃ by processes not yet understood, is characteristic of the Houston-Galveston Bay region during both spring and summer.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. INTRODUCTION</strong></td>
<td>11</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>11</td>
</tr>
<tr>
<td>1.2 SHARP 2009 Campaign Overview</td>
<td>12</td>
</tr>
<tr>
<td>1.3 Project Objectives</td>
<td>13</td>
</tr>
<tr>
<td><strong>2. DATA ANALYSIS (BY OBJECTIVE)</strong>*</td>
<td>15</td>
</tr>
<tr>
<td>2.1 Objective 1. Identify &amp; compare the variation of measured HOx and HO2/OH with NOx and VOCs.</td>
<td>15</td>
</tr>
<tr>
<td>2.1.1 Objective 1A: Comparison of observed and modeled HOx</td>
<td>15</td>
</tr>
<tr>
<td>2.1.2 Objective 1B: Observed-to-modeled ratios as a function of NO</td>
<td>18</td>
</tr>
<tr>
<td>2.1.3 Objective 1C: Observed-to-modeled ratios as a function of VOC reactivity</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Objective 2. Quantify &amp; compare observed and calculated OH reactivity to examine any missing OH sink species in the HOx Budget.</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Objective 3. Examine the significance of nighttime OH and determine the importance of O3 + alkenes and NO3 chemistry as nighttime OH sources</td>
<td>24</td>
</tr>
<tr>
<td>2.3.1 Objective 3A. Nighttime OH</td>
<td>24</td>
</tr>
<tr>
<td>2.3.2 Objective 3B. Importance of O3 + alkene reactions and NO3 chemistry as nighttime HOx sources</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Objective 4. Compare and contrast the HOx levels in Houston to those in Mexico, Nashville and New York City.</td>
<td>26</td>
</tr>
<tr>
<td>2.5 Objective 5. Investigate the impacts on instantaneous O3 production due to clouds and aerosols impacts and compare observed and calculated net O3 production.</td>
<td>28</td>
</tr>
<tr>
<td>2.5.1 Deviations in O3 production due to clouds and aerosols</td>
<td>28</td>
</tr>
<tr>
<td>2.5.2 Comparison of MOPS measured ozone production rate with model calculations</td>
<td>37</td>
</tr>
<tr>
<td>2.6 Objective 6. Study the sensitivity of O3 production to NOx and VOCs.</td>
<td>41</td>
</tr>
<tr>
<td>2.7 Objective 7. Investigate the potential of HONO as a daytime precursor of OH.</td>
<td>43</td>
</tr>
<tr>
<td>2.7.1 Objective 7A. Importance of HONO in HOx budget</td>
<td>43</td>
</tr>
<tr>
<td>2.7.2 1-D Box Modeling of daytime HONO</td>
<td>44</td>
</tr>
<tr>
<td>2.8 Objective 8. Evaluate the role of ClNO2 as an early morning radical source and its contribution to ozone production.</td>
<td>53</td>
</tr>
<tr>
<td>2.9 Objective 9. Correlations between HNO3 and gas phase chloride, and their implications for coupled Cl and NOx chemistry in Houston</td>
<td>55</td>
</tr>
<tr>
<td><strong>3. PROJECT SUMMARY</strong></td>
<td>60</td>
</tr>
<tr>
<td><strong>4. REFERENCES</strong></td>
<td>60</td>
</tr>
<tr>
<td><strong>5. APPENDIX A - MEASUREMENT PROCEDURES (SHARP DATA COLLECTION)</strong></td>
<td>66</td>
</tr>
<tr>
<td>5.1 Analytical Methods</td>
<td>66</td>
</tr>
<tr>
<td>5.1.1 Meteorology</td>
<td>66</td>
</tr>
<tr>
<td>5.1.2 Basic Trace Gases (O3, CO, SO2, NOx, NOy)</td>
<td>67</td>
</tr>
<tr>
<td>5.1.3 Photolysis Rates</td>
<td>68</td>
</tr>
</tbody>
</table>
5.1.4 VOCs ............................................................................................................................. 69
5.1.5 HNO₃, HONO, soluble Cl............................................................................................ 69
5.1.6 HONO .......................................................................................................................... 69
5.1.7 OH, HO₂ ...................................................................................................................... 70
5.1.8 O₃, NO₂, SO₂, HCHO, HONO, NO₃ ............................................................ 72

5.2 Calibration Procedures .............................................................................................................. 73
5.2.1 Meteorology .................................................................................................................... 73
5.2.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NO₃) ....................................................... 73
5.2.3 Photolysis Rates ............................................................................................................ 74
5.2.4 VOCs ............................................................................................................................. 74
5.2.5 HNO₃, HONO, soluble Cl ............................................................................................ 74
5.2.6 HONO .......................................................................................................................... 75
5.2.7 OH, HO₂ ...................................................................................................................... 76
5.2.8 O₃, NO₂, SO₂, HCHO, HONO, NO₃ ............................................................ 76

6. APPENDIX B - QUALITY METRICS (QA/QC CHECKS) (SHARP DATACOLLECTION) ................................................................................................................................... 78
6.1 QC Checks .................................................................................................................................. 78
6.1.1 Meteorology .................................................................................................................... 78
6.1.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NO₃) ....................................................... 79
6.1.3 Photolysis Rates ............................................................................................................ 79
6.1.4 VOCs ............................................................................................................................. 80
6.1.5 HNO₃, HONO, soluble Cl ............................................................................................ 80
6.1.6 HONO .......................................................................................................................... 80
6.1.7 OH, HO₂ ...................................................................................................................... 81
6.1.8 O₃, NO₂, SO₂, HCHO, HONO, NO₃ ............................................................ 83

6.2 Acceptance Criteria .................................................................................................................... 83
6.2.1 Meteorology .................................................................................................................... 83
6.2.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NO₃) ....................................................... 83
6.2.3 Photolysis Rates ............................................................................................................ 83
6.2.4 VOCs ............................................................................................................................. 83
6.2.5 HNO₃, HONO, soluble Cl ............................................................................................ 84
6.2.6 HONO .......................................................................................................................... 84
6.2.7 OH, HO₂ ...................................................................................................................... 84
6.2.8 O₃, NO₂, SO₂, HCHO, HONO, NO₃ ............................................................ 84

7. APPENDIX C – INORGANIC AND ORGANIC SPECIES USED IN OH REACTIVITYCALCULATIONS (SECTION 2.2) ............................................................................................ 85
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1-1. Daytime photochemical Processes.</td>
<td>12</td>
</tr>
<tr>
<td>Figure 2-1. Time series of observed (red) and modeled (blue) OH (top) and HO₂ (bottom) during SHARP 2009. Modeled OH and HO₂ were calculated with the RACM2 mechanism.</td>
<td>16</td>
</tr>
<tr>
<td>Figure 2-2. Median diurnal variation of observed (black) and modeled OH (top) and HO₂ (bottom) during SHARP 2009. Modeled OH and HO₂ were from 5 different chemical mechanisms, including RACM2, CB05, LaRC, SAPRC07, and MCMv3.1.</td>
<td>17</td>
</tr>
<tr>
<td>Figure 2-3. The ratios of observed to model OH (top), HO₂ (middle), and HO₂/OH (bottom) as a function of NO. The lines indicate the median profiles as a function of NO. Modeled OH and HO₂ were calculated with the RACM2 mechanism.</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2-4. The ratios of observed to model OH (top), HO₂ (middle), and HO₂/OH (bottom) as a function of VOC reactivity (OHR-organic). The lines indicate the median profiles as a function of OHR-organic. Modeled OH and HO₂ were calculated with the RACM2 mechanism.</td>
<td>20</td>
</tr>
<tr>
<td>Figure 2-5. Time series of OH reactivity (1) from total modeled and measured species, (2) from measured species only, and (3) from measured inorganic species. Modeled total OH reactivity was calculated with the RACM2 mechanism.</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2-6. Mean diurnal variations of OH reactivity (1) from total modeled and measured species, (2) from measured species only, and (3) from measured inorganic species.</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2-7. Time series of HOₓ production from O₃ + alkenes reactions and from NO₃ chemistry. Modeled NO₃ from the RACM2 mechanism is used to calculate HOₓ production from NO₃ chemistry.</td>
<td>25</td>
</tr>
<tr>
<td>Figure 2-8. Median diurnal variations of HOₓ production from O₃ + alkenes reactions and from NO₃ chemistry. Modeled NO₃ from the RACM2 mechanism is used to calculate HOₓ production from NO₃ chemistry.</td>
<td>25</td>
</tr>
<tr>
<td>Figure 2-9. Diurnal variations of OH (top) and HO₂ (bottom) in Houston during SHARP 2009, in Mexico City during the Mexico City Metropolitan Area study (MCMA 2003), in New York City during the PM2.5 Technology Assessment and Characterization Study (PMTACS 2001), and in Nashville during the Southern Oxidation Study (SOS99).</td>
<td>27</td>
</tr>
<tr>
<td>Figure 2-10. Measured O₃ and j(NO₂), and instantaneous net P(O₃) with measured and modeled j(NO₂) for a low and high O₃ day.</td>
<td>28</td>
</tr>
<tr>
<td>Figure 2-11. Histogram of j(NO₂) JIF during SHARP for six cloud free days and 42 days with cloud impacts.</td>
<td>29</td>
</tr>
<tr>
<td>Figure 2-12. Peak net P(O₃) occurs at JIFs of ~0.75 or greater. Below JIFs of 0.75 net P(O₃) decreases with JIF.</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 2-13. Net P(O₃) varies nearly 1:1 with reductions in j(NO₂)..........................30

Figure 2-14. Average O₃ formation rates for all days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). .........................31

Figure 2-15. Average O₃ rates for high O₃ days (greater than 65 ppbv for 8-hr average). Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). ..............................................................32

Figure 2-16. Average O₃ rates for low O₃ days (less than 40 ppbv for 8-hr average). Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). .................................................................................................32

Figure 2-17. Median diurnal O₃ formation rate for all days and the selected high and low O₃ days. Solid lines represent calculations with CFM j(NO₂), broken lines represent calculations with SAFS j(NO₂)..........................................................33

Figure 2-18. Median diurnal profile of O₃ formation terms for the selected high O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). .................................................................34

Figure 2-19. Median diurnal profile of O₃ formation terms for the selected low O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). .................................................................................................34

Figure 2-20. Median diurnal profile of O₃ destruction terms for the selected high O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). .................................................................................................35

Figure 2-21. Median diurnal profile of O₃ destruction terms for the selected low O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂). .................................................................................................36

Figure 2-22. Median diurnal O₃ profiles for TRAMP (August & September 2006) and SHARP (April & May 2009). Production rates for CFM and SAFS j(NO₂) are shown in solid and broken lines, respectively. ..................................................36

Figure 2-23. Time series from 19 April (day 119) to 30 May (day 150), 2009 for ambient ozone (green dots), calculated P(O₃) from ancillary measurements (black circles), measured P(O₃) with the MOPS (blue dots) and modeled P(O₃) from the RACM2 mechanism (red dots). ..........................................................38

Figure 2-24. Measured P(O₃) in NO space for the high ozone episode that started on 19 May, developed on 20 May and subsided on 21 May, 2009 in Houston. The color scale corresponds to hour of the day. The number on top of every curve is the date in May..........................................................39

Figure 2-25. P(O₃) in NO space (a) measured by the MOPS, (b) calculated and (c) modeled for overlapping points only and daylight hours. The color scale corresponds to hour of the day..........................................................40

Figure 2-26. Median diurnal profiles of L₉/Q in TEXAQS 2000, TRAMP 2006, and SHARP 2009..........................................................42
Figure 2-27. Diurnal variation of HOx production (top) and HOx loss (bottom). HOx production processes include ozone photolysis followed by the O1D + H2O reaction, the photolysis of HONO, the photolysis of HCHO, and ozone reactions the alkekens. HOx loss processes include OH reaction with NOx, HO2+HO2 reaction and HO2 + RO2 reactions. RACM2 modeled results are used. .................................................. 43

Figure 2-28. Timeseries of meteorological data, JNO2, NO, OH, HONO, NO2 and HONO to NO2 ratio on April 21, 2009. LP-DOAS HONO, NO2, and HONO/NO2 data are color codes by altitude interval: lower 20-70m, middle: 70-130m, and upper: 130-300m. HONO and NO2 data after 9:00 CST are displayed with different scales on the right y-axis. Error bars of one standard deviation are shown on NO2, HONO and HONO/NO2. Please note that the OH data shown here is the average of OH observed during sunny days in Houston............................................................ 45

Figure 2-29. Timeseries of HONO formation and removal rates at the lower height interval on April 21, 2009 (left) and May 18, 2009 (right). Please note that errors were propagated from the statistical uncertainties in the observations............................................... 46

Figure 2-30. Timeseries of Pnorm in the lower and middle height intervals on April 21, 2009 (left) and May 18, 2009 (right). Pnorm in the upper height intervals was not calculated due to insufficient data. Photolysis frequency of NO2 and solar irradiance are shown as well for comparison................................................................................. 46

Figure 2-31. Correlations between Pnorm and JNO2 (panel a) and solar visible irradiance (panel b) at lower and middle height intervals on four sunny days (April 21, May 4, May 18 and May 19) during SHARP 2006. Results of the linear fits are shown in Table 2-3.......................................................... 48

Figure 2-32. OH production rates on three sunny days in Houston during the SHARP 2009 experiment. Shows are the rates in three different height intervals: low (20-70m), (mid) 70-130m and (up) 130-300m. ..................................................................................... 50

Figure 2-33. Comparisons of daytime HONO, NO2 and [HONO]/[NO2] ratios between observations and different model simulations on April 21, 2009.............................................. 51

Figure 2-34. Model results in a base run with RACM2 plus chlorine chemistry. The model was constrained by measured ClNO2 and HCl without additional Cl sources. .......................................................... 53

Figure 2-35. Model results in a sensitivity run with RACM2 plus chlorine chemistry. The model was constrained by measured ClNO2 and HCl and a constant [Cl2] of 20 pptv.................................................................................................... 53

Figure 2-36. Model results in a sensitivity run with RACM2 plus chlorine chemistry. The model was constrained by measured ClNO2 and HCl and a constant [Cl2] of 100 pptv.................................................................................................... 53

Figure 2-37. Time series of soluble chloride gas (which is thought to be gaseous HCl) and HNO3 during SHARP campaign.............................................................. 55

Figure 2-38. Time series of soluble chloride gas (which is thought to be gaseous HCl) and HNO3 during SHARP campaign during a relatively clean period (April 24-26th 2009) during period of southerly air flow. Note the higher ratio between gaseous chloride and HNO3 and striking covariation in daytime.............................................................. 56
Figure 2-39. Time series of soluble chloride gas and HNO$_3$ during SHARP campaign during a relatively polluted period (May 29-30th 2009) during period of northerly air flow. Note the lower ratio between gaseous chloride and HNO$_3$ and the very large differences in scaling between Figure 2-38 and Figure 2-39. Yet chloride and nitric acid still have very strong covariance.

Figure 2-40. Hourly mean diurnal mixing ratios of HNO$_3$ (top) and soluble Cl$^-$ (bottom) during SHARP. Nighttime enhancements of HNO$_3$, but not soluble Cl$^-$ occurred fairly frequent during SHARP. This suggests an alternative HNO$_3$ production pathway, perhaps through N$_2$O$_5$.

Figure 2-41. Relative abundance of soluble gaseous Cl$^-$ compared to HNO$_3$ during SHARP of all days (top). Same ratio plotted as a function of wind direction. Note large increase in soluble gaseous Cl$^-$ during southerly flow.
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2-1. Mean concentrations of observed and modeled OH during SHARP (units: pptv)</td>
<td>17</td>
</tr>
<tr>
<td>Table 2-2. Mean concentrations of observed and modeled HO2 during SHARP (units: pptv)</td>
<td>17</td>
</tr>
<tr>
<td>Table 2-1. Linear fits results of Figure 2-22</td>
<td>48</td>
</tr>
<tr>
<td>Table 5-1. Overview of the measurements within project H104C during the 2009 SHARP experiment</td>
<td>72</td>
</tr>
<tr>
<td>Table 5-2. Detection limits for trace gases measured by UCLA’s LP-DOAS during SHARP in Houston, 2009</td>
<td>77</td>
</tr>
<tr>
<td>Table 6-1. QA/QC checks for the O3, CO, SO2, NO, NO2, and NOy measurements</td>
<td>79</td>
</tr>
<tr>
<td>Table 6-2. QA/QC checks for the VOC measurements</td>
<td>80</td>
</tr>
<tr>
<td>Table 6-3. Regular maintenance work</td>
<td>82</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

1.1 Background

The chemistry of atmospheric radicals, especially the hydroxyl radical (OH) and hydroperoxyl radical (HO$_2$), together called HO$_x$, is deeply involved in the formation of the secondary pollutants ozone and fine particles. OH initiates most reaction sequences that cycle surface emissions through the atmosphere. HO$_2$ is readily exchanged with OH. In the exchange process, HO$_2$ reacts with NO to form OH and NO$_2$, leading to ozone formation. Understanding these chemical processes will be important in determining the extent and types of emission reductions that will be most effective in reducing ozone. Predictive capability for ozone and its response to regulatory action requires a firm understanding of HO$_x$ sources, sinks, and interactions with anthropogenic hydrocarbons and nitrogen oxides.

Radical precursors such as nitrous acid (HONO) and formaldehyde (HCHO) significantly affects HO$_x$ budget in urban environments like Houston. These chemical processes connect surface emissions, both human and natural, to local and regional pollution, and climate change. During the Study of Houston Atmospheric Radical Precursors (SHARP) in spring 2009, a relatively complete suite of measurements, including OH and HO$_2$ mixing ratios, ozone production rates, and other ozone precursors, were performed. This provides us a unique opportunity to examine and improve the understanding of atmospheric oxidation and ozone and fine particle formation processes. The analysis of SHARP data will strengthen the understanding of atmospheric oxidation and air quality and development of the SIP, which is essential to meet the new primary and secondary National Ambient Air Quality Standards for ozone.

Although portions of the chemistry that lead to the formation of ozone have been understood for decades, new discoveries have revealed the need to improve scientific understanding of ozone formation chemistry [Texas Air Quality Research Program, 2010]. Radical production in Houston and other urban areas appear to be underestimated by chemical mechanisms. Some gas-phase and heterogeneous chemical reactions seem missing from the mechanisms. The roles of some radical precursors such as HONO, HCHO, and reactive volatile organic compounds (VOCs) in ozone formation in Houston and other Texas cities have not been well understood [Texas Air Quality Research Program, 2010].

Previous studies have shown the importance of both anthropogenic and natural hydrocarbons in this environment. Knowledge of these HO$_x$ sources and sinks will be important for defining the oxidation and ozone formation processes in this urban plume. Further, in the morning when NO is high, observed HO$_2$ is larger than modeled HO$_2$. Because ozone production is the product of [NO] and [HO$_2$], ozone production calculated from observations is much greater than modeled ozone production.

In addition, the contribution that nitrous acid (HONO) makes as a daytime source of NO and OH, and the potential role of ClNO$_2$ as an additional early morning source of radicals has previously been neglected in SIP and other 0-D and 1-D models of air quality in Houston. Comparison of observed HONO with simulations made by several photochemical models can assess the magnitude of poorly constrained heterogeneous production mechanisms. Investigation of ClNO$_2$, gaseous HNO$_3$ and soluble Cl (thought to be HCl) can reveal the apparent importance of transport controlling linked variations of HNO$_3$ and Cl$. As part of this project, Cl chemistry has been implemented into one of the photochemical model mechanism to assess its impact on radical budgets and ozone levels in the atmosphere of Houston.
Figure 1-1 describes in principle the fast reaction cycles involved in the formation of secondary species as well as the removal mechanisms from those cycles for nitrogen and carbon containing species. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and controls the atmospheric lifetimes of most trace gases. OH is produced in photolysis processes of ozone (O$_3$), formaldehyde (HCHO) and nitrous acid (HONO). OH initiates oxidation reactions with NO$_x$, CO, anthropogenic and biogenic VOCs. These reactions form peroxy radicals (RO$_2$) which in turn will cause the conversion of NO to NO$_2$ and subsequently the formation of O$_3$. Within the degradation of VOC also carbonyls will be formed which either may be photolyzed (e.g. formaldehyde) or oxidized by OH and finally contribute to the formation of peroxycarboxylic nitric anhydrides (PANs). Loss mechanisms for OH involve reactions between peroxy radicals leading to hydrogen peroxide (H$_2$O$_2$) and organic peroxides, e.g. methylhydroperoxide (MHP) and hydroxylmethylhydroperoxide (HMHP), and reactions with NO$_2$ leading to nitric acid (HNO$_3$) and PAN. Critical uncertainties of the processes described in Figure 1-1 are associated with the direct emissions of the OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources, as well as from mobile sources. For HONO, surface-induced formation of HONO, possibly linked to the previous deposition of HNO$_3$, has not yet been sufficiently investigated. Closely related to this latter issue is the fact that daytime HONO levels and its sources are not well understood.

1.2 SHARP 2009 Campaign Overview

The SHARP campaign (April 15 – May 31, 2009) was designed to examine the processes involved in the springtime ozone peak observed in southeast Texas. Chemical and meteorological measurements were made from a height of 70 m above ground level (a.g.l.) at the top of a 10 m tower on a roof balcony of the north Moody Tower, an 18-story dormitory on the campus of the University of Houston. Prior to the 2006 TRAMP campaign conducted at this site, several small laboratories were constructed on the roof balcony of the north Moody Tower and significant power was added to support research instrumentation. The permanent
10-meter mast tower was erected on the site for measurement equipment and inlets. For the SHARP campaign in 2009, a temporary 6-meter walk-up scaffold tower and temporary laboratory were erected on the balcony to accommodate the additional needs of the visiting scientists.

The UH main campus is 35 km west of Galveston Bay, 70 km NW of Galveston, TX and the Gulf of Mexico. The north Moody Tower (29.7176 °N, −95.3413 °W) on the University of Houston main campus is located in a partially wooded and grass covered land surface approximately 5 km southeast of tall buildings in “downtown” Houston, 1 km southwest of Interstate 45, and 3.5 km north of the South Interstate 610 Loop. The measurement site is 6 km southwest of the Buffalo Bayou Turning Basin and 25 km west-southwest of the San Jacinto Battleground Monument, the western and eastern edges, respectively of the petrochemical facilities in the Houston Ship Channel. The primary difference between the Moody Tower “supersite” and other measurement datasets is that the SHARP dataset is a series of continuous 24 hours per day, 7 days per week measurements (including quality control samples, as deemed appropriate by the investigator) for more than 6 weeks at a site 70 m a.g.l. This is unique because all other surface sampling sites are much more sensitive to the nearby (i.e., within 100 m) local activities such as: traffic, parking lots, delivery trucks, railways, nocturnal surface drainage, etc. The following table lists the measurements made at the site that will be used in this analysis project. All measurements made during the campaign were recorded with synchronized timestamps and were matched with corresponding meteorological parameters. The data used in this project will be provided in a format suitable for use in a database.

1.3 Project Objectives

The TexAQS-II Radical and Aerosol Measurement Project (TRAMP, 2006) and SHARP (2009) projects have identified major uncertainties in our understanding of the radical budget in Houston. These include primary emissions of nitrous acid (HONO) and formaldehyde (HCHO) from point sources as well as from area sources including surface related processes for the formation of HONO. Another important uncertainty was found in daytime HONO levels. A better quantification of these OH sources is needed to improve the description of ozone (O₃) chemistry in air quality models in Houston. The accurate description of ozone chemistry is required to develop efficient strategies to reduce pollution in Houston and to develop the Houston–SIP.

The AQRP SHARP Data Analysis project (10-032) is designed to address the following objectives:

Objective 1. Identify the variation of measured HOₓ and HO₂/OH with NOₓ and VOCs and compare to the model prediction.

Objective 2. Quantify OH reactivity and compare observed and calculated OH reactivity to examine any missing OH sink species.

Objective 3. Examine the significance of nighttime OH and determine the importance of both the reaction of O₃ + alkenes and NO₃ chemistry as nighttime OH sources.

Objective 4. Compare and contrast the HOₓ levels in Houston to those in Mexico, Nashville and New York City.

Objective 5. Investigate the instantaneous O₃ production and deviations of the NOₓ photostationary state due to clouds and aerosols. This analysis will also include
comparison of observed and calculated HO$_2$ + RO$_2$ mixing ratios and net O$_3$
production.

Objective 6. Study the sensitivity of O$_3$ production to NO$_x$ and VOCs.

Objective 7. Investigate the potential of HONO as a daytime precursor of OH.

Objective 8. Evaluate the role of ClNO$_2$ as an early morning radical source and its’
contribution to ozone production.

Objective 9. Investigate the processes creating strong correlations between HNO$_3$ and
gas phase chloride, and their implications for coupled Cl and NOx chemistry in
Houston.

In order to address these research issues, in-depth data analysis of the SHARP dataset was
conducted with the expectation of leading to peer reviewed publications in the winter of
2011/12.
2. DATA ANALYSIS (BY OBJECTIVE)

In this project, the SHARP Data Analysis team applied a photochemical model with five different chemical mechanisms for the SHARP 2009 Moody Tower (Houston) springtime chemical data set. The five chemical mechanisms used in this study include Regional Atmospheric Chemistry Mechanism Version 2 (RACM2, Stockwell et al., 1997; Goliff and Stockwell, 2008), Carbon Bond Mechanism Version 2005 (CB05) (Yarwood et al., 2005), a chemical Mechanism developed by NASA Langley Research Center (LaRC, Crawford et al., 1999), Statewide Air Pollution Research Center Version 2007 (SAPRC07, Carter, 1996; 2007), and Master Chemical Mechanism Version 3.1 (MCMv3.1, Jenkin et al., 2003; Sanders et al., 2003; Bloss et al., 2005). The complete VOC data set was received at the end of June, 2011. Input files for these mechanisms were created and the model mechanisms were updated to the available constrained chemical and meteorological parameters. Model simulations with the various mechanisms were completed and results are summarized below.

2.1 Objective 1. Identify & compare the variation of measured HO\textsubscript{x} and HO\textsubscript{2}/OH with NO\textsubscript{x} and VOCs.

2.1.1 Objective 1A: Comparison of observed and modeled HO\textsubscript{x}

Two approaches were adopted for measuring OH and HO\textsubscript{2} during SHARP. One was the traditional wavelength modulation using the difference in the on-line and off-line signals. The measured OH in this approach is called “OH\textsubscript{wave}”. The second approach was to measure OH by chemical modulation using the difference in the signal with and without an overwhelming addition of high-purity gaseous perfluoropropene (C\textsubscript{3}F\textsubscript{6}). C\textsubscript{3}F\textsubscript{6} is an ideal gas for OH scrubber, as it is fast enough to remove OH in milliseconds without propagating radicals or complicating secondary chemistry. Its absorption around 308 nm is also negligible. The signal difference between with and without addition of C\textsubscript{3}F\textsubscript{6} is called “OH\textsubscript{chem}”.

Laboratory studies have also found that the organic peroxy radicals originating from alkenes can cause interferences in the HO\textsubscript{2} measurements. It was found that about 60% of those alkene RO\textsubscript{2} radicals are detected as HO\textsubscript{2}. Therefore the true HO\textsubscript{2} concentrations are derived from HO\textsubscript{2} wave subtracted by 60% of calculated alkene RO\textsubscript{2} radicals. The corrected HO\textsubscript{2} data was used in the following analysis.

As shown in Figure 2-1 and Figure 2-2, the measured and model OH and HO\textsubscript{2} exhibit similar diurnal and day-to-day variations, with maxima in the early afternoon and minima at night.
The comparison of observed and modeled OH and \( \text{HO}_2 \) mean concentrations is summarized in Table 2-1 and Table 2-2. In general, the models reproduced the observed OH and \( \text{HO}_2 \) with all 5 mechanisms producing similar levels of OH and \( \text{HO}_2 \), although CB05 produced slightly more \( \text{HO}_2 \) than others. The daytime OH was over-predicted and nighttime OH and \( \text{HO}_2 \) are both under-predicted. Comparing the observed OH and \( \text{HO}_2 \) with the RACM2 simulation, the median daytime observed-to-modeled OH ratio is 0.84 and the median daytime observed-to-modeled \( \text{HO}_2 \) ratio is 1.49. The differences among the 5 mechanisms are mainly due to the different treatments of VOCs because each mechanism has a very similar inorganic reaction scheme, i.e., MCM has an explicit VOC reaction scheme, while all other 4 mechanisms have lumped VOC species with different function groups. Similar comparison results were found for TRAMP 2006 (Chen et al., 2010).

Using the composite diurnal values in 1-hour bins, independent-sample t-tests (Student’s t-tests) were conducted to see if there are significant differences between the measurements and model calculations. A t-test result with a p-value (significance) greater than 0.05 is considered to be not significantly different between the two samples. The t-test results for the measured and modeled OH show that the p-values are 0.62 for RACM2, 0.41 for CB05, 0.98 for LaRC, 0.79 for SAPRC07, and 0.75 for MCMv3.1. The results for the measured and modeled \( \text{HO}_2 \) show the p-values of 0.19 for RACM2, 0.98 for CB05, 0.13 for LaRC, 0.46 for SAPRC07, and 0.09 for MCMv3.1. All these t-tests were conducted at a 95% confidence level and suggest that while the measurements and calculations are overall not significantly different, the nighttime differences are. Considering the p-values in the t-tests for both OH and \( \text{HO}_2 \), CB05 and SAPRC07 seem to perform better than other mechanisms in terms of OH and \( \text{HO}_2 \) simulations during SHARP.
Figure 2-2. Median diurnal variation of observed (black) and modeled OH (top) and HO2 (bottom) during SHARP 2009. Modeled OH and HO2 were from 5 different chemical mechanisms, including RACM2, CB05, LaRC, SAPRC07, and MCMv3.1.

Table 2-1. Mean concentrations of observed and modeled OH during SHARP (units: pptv)

<table>
<thead>
<tr>
<th></th>
<th>Obs, (mean±σ)</th>
<th>RACM2 (mean±σ)</th>
<th>CB05 (mean±σ)</th>
<th>LaRC (mean±σ)</th>
<th>SAPRC07 (mean±σ)</th>
<th>MCMv3.1 (mean±σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Data</td>
<td>11.2±10.5</td>
<td>8.0±8.1</td>
<td>10.4±10.5</td>
<td>7.4±9.1</td>
<td>9.0±9.4</td>
<td>6.9±8.5</td>
</tr>
<tr>
<td></td>
<td>min: 0.041</td>
<td>min: 0.014</td>
<td>min: 0.013</td>
<td>min: 0.012</td>
<td>min: 0.035</td>
<td>min: 0.010</td>
</tr>
<tr>
<td></td>
<td>max: 63.9</td>
<td>max: 45.8</td>
<td>max: 49.5</td>
<td>max: 49.0</td>
<td>max: 52.8</td>
<td>max: 45.0</td>
</tr>
<tr>
<td>Day</td>
<td>15.3±12.5</td>
<td>11.9±9.7</td>
<td>15.4±12.5</td>
<td>12.2±10.7</td>
<td>13.5±11.2</td>
<td>11.8±9.7</td>
</tr>
<tr>
<td>Night</td>
<td>6.9±5.5</td>
<td>3.9±2.0</td>
<td>5.2±2.7</td>
<td>2.4±1.7</td>
<td>4.3±2.3</td>
<td>1.8±1.0</td>
</tr>
</tbody>
</table>

Table 2-2. Mean concentrations of observed and modeled HO2 during SHARP (units: pptv)
Key Findings:

- In general, the models reproduced the observed OH and HO\textsubscript{2} with all 5 chemical mechanisms producing similar levels of OH and HO\textsubscript{2}
- CB05 produced slightly higher HO\textsubscript{x} than measured and significantly less OH than the others
- Given that HO\textsubscript{2} is approximately 20 times higher than OH during the day, the CB05 model predicted the closest total HO\textsubscript{x} of all five mechanisms
- The results suggesting that not much modeling skill has been lost by employing lumped VOC reaction schemes in the regional chemical transport models used for SIP evaluations

2.1.2 Objective 1B: Observed-to-modeled ratios as a function of NO

The observed-to-modeled OH and HO\textsubscript{2} ratios can test our understanding of the HO\textsubscript{x} photochemistry because the cycling between OH and HO\textsubscript{2} is very fast and the photochemical equilibrium among OH and HO\textsubscript{2} is closely tied to the interconversion of NO and NO\textsubscript{2} in the troposphere. The average model results from the five mechanisms tends to underpredict OH when NO is less than a few hundred pptv or NO is greater than a few ppbv, while the modeled OH agrees well with measurements when NO is between a few hundred pptv and a few ppbv (Figure 2-3, top). For HO\textsubscript{2}, the observed-to-modeled ratio is fairly constant when NO is below a few ppbv, while the ratio increases as NO increases (Figure 2-3, middle), as has been observed in previous field studies in other cities. Note that the average model results from the five mechanisms were used in Figure 2-3 as an example. The model result from each individual mechanism shows the same behaviors as a function of NO.

Both the measured and modeled HO\textsubscript{2}/OH ratios decrease with increasing NO (Figure 2-3, bottom). This decrease occurs because NO shifts HO\textsubscript{2} into OH by reacting with HO\textsubscript{x}. However, when NO is lower than a few hundred ppbv, the modeled HO\textsubscript{2}/OH ratios are significantly higher than the measured. The agreement of measured and modeled HO\textsubscript{2} to OH ratios is good when NO is around a few hundred pptv. The slope of measured HO\textsubscript{2}/OH as a function of NO is significantly less than the modeled slope. This difference is consistent with measured OH being greater than modeled OH at low NO, while measured HO\textsubscript{2} is much greater than modeled HO\textsubscript{2} at high NO (Figure 2-3).
Key Findings:
- The average model results from the five mechanisms predicted OH agrees well with measurements at moderate NO levels but underpredicts OH at both lower and higher NO levels.
- The observed-to-modeled ratio for HO2 is fairly constant around 2, however the measurement/model agreement significantly deteriorates at “high” NO mixing ratios.

2.1.3 Objective 1C: Observed-to-modeled ratios as a function of VOC reactivity

In addition to NO, VOCs also play important roles in HOx chemistry. VOCs react with OH to act as OH sinks and to produce organic peroxy radicals, RO2. In the presence of NO, RO2 reacts with NO to produce NO2 and HO2. The model (with RACM2 mechanism) tends to underpredict OH when VOC reactivity is greater than 5-10 s⁻¹ or less than 3 s⁻¹, while the modeled OH agrees generally well with measurements when VOC reactivity is around 5 s⁻¹ (Figure 2-4, top). For HO2, the observed-to-modeled ratio is close to 1 and fairly constant in the entire range of VOC reactivity (Figure 2-4, middle).

The correlation between observed and modeled HO2/OH ratio as a function of VOC reactivity is mixed. The observed HO2/OH ratio is fairly constant for the entire range of VOC reactivity, while modeled HO2/OH ratio is greater than the observed ratio when the VOC reactivity is less than or greater than 4-5 s⁻¹ (Figure 2-4, bottom). This difference is consistent with measured OH being greater than modeled OH at low or high VOC reactivity.
Figure 2-4. The ratios of observed to model OH (top), HO$_2$ (middle), and HO$_2$/OH (bottom) as a function of VOC reactivity (OHR-organic). The lines indicate the median profiles as a function of OHR-organic. Modeled OH and HO$_2$ were calculated with the RACM2 mechanism.

Key Findings:

- The RACM2 mechanism tends to underpredict OH when VOC reactivity is > 5-10 s$^{-1}$ or < 3 s$^{-1}$, while the modeled OH agrees generally well with measurements when VOC reactivity is $\sim$5 s$^{-1}$
- The observed HO$_2$/OH ratio is fairly constant for the entire range of VOC reactivity, while modeled HO$_2$/OH ratio is greater than the observed ratio when the VOC reactivity is less than or greater than 4-5 s$^{-1}$
2.2 Objective 2. Quantify & compare observed and calculated OH reactivity to examine any missing OH sink species in the HOx Budget.

Unfortunately the fiber optics used for the measurements of OH reactivity during the SHARP campaign repeatedly failed. For some unknown reason UV transmission of the new batch of fiber optic cables purchased for the SHARP campaign rapidly degraded to become unusable. Various attempts to rectify this problem including repeated re-cutting and polishing of fiber ends, changes in laser intensity, etc did not rectify the problem. Conversation with the fiber manufacturer did not shed any light on the source of the problem as fibers with the identical part number worked well in the past. Initial attempts during the project to recover some OH reactivity data when the fibers had just been repaired were not successful as the fiber transmission degraded faster than anticipated. As a result of the fiber transmission problems there are little to no observed OH reactivity data. Consequently, the only OH reactivity reported here are the calculated OH reactivity determined from measured species (where available) and modeled species (using a photochemical box model using the RACM2 mechanism) when measurements of a particular reactive species was not available.

The calculated inorganic OH reactivity was determined using the species specific OH rate constant and the measured concentrations of the following measured inorganic compounds: O₃, CO, NO, NO₂, HNO₃, HOOH, HONO, and SO₂. The measured organic OH reactivity was calculated from the measured abundances of the following compounds: CH₄ (not measured but assumed to be 2 ppm), ETH (ethane), ETE (ethylene), HC₃ (other alkanes, alcohols, esters and alkenes with OH rate constant (298 K, 1 atm) less than 3.4x10⁻¹² cm³ s⁻¹), HC₅ (other alkanes, alcohols, esters and alkenes with OH rate constant (298 K, 1 atm) between 3.4x10⁻¹² and 6.8x10⁻¹² cm³ s⁻¹), HC₈ (other alkanes, alcohols, esters and alkenes with HO rate constant (298 K, 1 atm) greater than 6.8x10⁻¹² cm³ s⁻¹), ISO (Isoprene), TOL (toluene and less reactive aromatics), OLT (terminal alkenes), ACE, OL, XYO, LIM, HCHO, ALD, MEK, HACET, UALD, GLY, MGLY, DCB1, DCB2, DCB3, BALD, PHEN, CSL, EPX, MCT, EOH, ROH, ETLEG, OP1, OP2, ISHP, MAHP, ORA1, ORA2, MPAN, ONIT, NALD, and ISON. Species that were not measured or were not continuous measurement were modeled for the calculation of OH reactivity include the following: NO₃, HO₂, NO₂, DIEN, ACE, OL, XYO, LIM, HCHO, ALD, MEK, HACET, UALD, GLY, MGLY, DCB1, DCB2, DCB3, BALD, PHEN, CSL, EPX, MCT, EOH, ROH, ETLEG, OP1, OP2, ISHP, MAHP, ORA1, ORA2, MPAN, ONIT, NALD, and ISON. A summary table of these species used and their description can be found in Section 7 – Appendix C.
Figure 2-5. Time series of OH reactivity (1) from total modeled and measured species, (2) from measured species only, and (3) from measured inorganic species. Modeled total OH reactivity was calculated with the RACM2 mechanism.

As shown in Figure 2-5, total OH reactivity calculated from measured and model species and the OH reactivity from measured species are about the same, indicating that modeled intermediates do not contribute too much to the OH reactivity. This suggests that a relative complete suite of measurements during SHARP.

Figure 2-6. Mean diurnal variations of OH reactivity (1) from total modeled and measured species, (2) from measured species only, and (3) from measured inorganic species.

Diurnal profile of OH reactivity show that peak OH reactivity appeared in the early morning, as expected from previous campaigns (Figure 2-6). On average, the OH reactivity from measured species account for about 94% of the total calculated OH reactivity.
Key Findings:

- The calculated OH reactivity from measured species account for about 94% of the total calculated OH reactivity.
- The results indicate that modeled organic intermediates do not contribute significantly to the OH reactivity, i.e. there does not appear to have been any appreciable “missing” OH reactivity.
2.3 Objective 3. Examine the significance of nighttime OH and determine the importance of O₃ + alkenes and NO₃ chemistry as nighttime OH sources.

2.3.1 Objective 3A. Nighttime OH

Studies have found that in the planetary boundary layer two oxidation pathways can contribute to HOₓ production at night: (1) O₃ reactions with alkenes to produce a significant amount of OH and HO₂ and (2) NO₃ reactions with a few VOCs such as HCHO, unsaturated aldehydes, methacrolein, and glyoxal to produce HOₓ directly or with RO₂ that is initially produced by VOCs+NO₃. These processes become more important for the nighttime HOₓ production because daytime HOₓ photolytic sources vanish at night.

The mean measured nighttime OH concentration is 0.043 pptv or 1.0x10⁶ molecules cm⁻³, while the modeled nighttime OH concentration (averaged value from the 5 different mechanisms) is 0.0064 pptv or 1.6x10⁵ molecules cm⁻³ (Table 2-1 and 2-2). The mean measured nighttime HO₂ is 6.9 pptv, while the modeled nighttime HO₂ concentration (averaged value from the 5 different mechanisms) is 3.5 pptv (Table 2-1 and Table 2-2). This indicates that OH and HO₂ may also play important roles in the nighttime oxidation chemistry. The model underpredicts both nighttime OH and HO₂ (Figure 2-2, Table 2-1 and Table 2-2). The median measured-to-modeled HO₂ ratio at night is 1.54, which is within the combined uncertainty of measured and modeled HO₂. The median measured-to-modeled OH ratio at night is 4.46, which is significantly beyond the combined uncertainty of the measured and modeled OH. This difference indicates that all mechanisms fail to capture the processes that create nighttime OH in this urban environment.

Key Finding:
- All of the tested mechanisms fail to capture the processes that create nighttime OH in this urban environment

2.3.2 Objective 3B. Importance of O₃ + alkene reactions and NO₃ chemistry as nighttime HOₓ sources.

Figure 2-7 shows the time series of HOₓ production from O₃ + alkene reactions and from NO₃ chemistry. As expected, typical diurnal variations of HOₓ production from these two pathways were obtained. HOₓ production from O₃ + alkene reactions peaks in the midday when O₃ concentration is highest, while HOₓ production from NO₃ chemistry peaks at night because of low NOₓ concentrations during the day due to its fast photolysis. In general, NOₓ chemistry contributes less HOₓ production than the O₃ + alkene reaction, except for a few nights (e.g., the night of May 20 and 21) when NOₓ concentrations were high. On these occasions, O₃ mixing ratios were higher than NOₓ consequently as NO titrated O₃, the resulting NOₓ reacted with the remaining O₃ to produce high concentrations of NOₓ. Modeled NOₓ concentrations are used in the calculation due to the low data coverage in the DOAS NOₓ measurements. In general, the modeled NOₓ is in good agreement with observed NOₓ, with the modeled NOₓ being slightly lower than the observed NOₓ, but within the uncertainty of the observations.
Figure 2-7.  Time series of HO\textsubscript{x} production from O\textsubscript{3} + alkenes reactions and from NO\textsubscript{3} chemistry versus day of year (30 April – 1 June 2009).  Modeled NO\textsubscript{3} from the RACM2 mechanism is used to calculate HO\textsubscript{x} production from NO\textsubscript{3} chemistry.

On average, the nighttime HO\textsubscript{x} production rate from O\textsubscript{3}+alkene reactions is about 5.7 x 10\textsuperscript{5} molecules m\textsuperscript{-3} s\textsuperscript{-1}, or 84.0 pptv hr\textsuperscript{-1}, while NO\textsubscript{3} chemistry contributes about 2.6 x 10\textsuperscript{5} molecules m\textsuperscript{-3} s\textsuperscript{-1}, or 38.8 pptv hr\textsuperscript{-1} (Figure 2-8).  Nighttime HO\textsubscript{x} production from O\textsubscript{3}+alkene reactions contributes about 68% of the total, with the remainder coming from NO\textsubscript{3} chemistry.

Figure 2-8.  Median diurnal variations of HO\textsubscript{x} production from O\textsubscript{3} + alkenes reactions and from NO\textsubscript{3} chemistry.  Modeled NO\textsubscript{3} from the RACM2 mechanism is used to calculate HO\textsubscript{x} production from NO\textsubscript{3} chemistry.
Key Findings:

- During SHARP, NO₃ chemistry contributed less (32%) HOₓ production than the O₃ + alkene reactions (68%) on most nights.
- Long path DOAS measurements during SHARP indicate that there is significant NO₃ formation at higher altitudes where lower nighttime NO levels are observed.

2.4 Objective 4. Compare and contrast the HOₓ levels in Houston to those in Mexico, Nashville and New York City.

Compared to the OH and HO₂ measurements in three other cities (Mexico City, New York City and Nashville, TN) the measured OH concentrations in Houston during SHARP are comparable to the OH measurements in other cities (Figure 2-9, top), indicating that the OH production and loss rate are generally well buffered. However, the peak HO₂ concentration in Mexico City is the highest (Figure 2-9, bottom), while the HO₂ concentrations in New York City are the lowest, simply because of the high NOₓ concentrations in New York City throughout the day. HO₂ levels in Houston are more or less like those in Nashville.
Figure 2-9. Diurnal variations of OH (top) and HO$_2$ (bottom) in Houston during SHARP 2009, in Mexico City during the Mexico City Metropolitan Area study (MCMA 2003), in New York City during the PM2.5 Technology Assessment and Characterization Study (PMTACS 2001), and in Nashville during the Southern Oxidation Study (SOS99).

Key Findings:
- OH concentrations in Houston during SHARP are comparable to other cities
- Springtime HO$_2$ levels in Houston are more or less like those in Nashville
- The similarity of OH levels in these cities indicates that the OH production and loss rate are well buffered in urban environments
2.5 Objective 5. Investigate the impacts on instantaneous O$_3$ production due to clouds and aerosols impacts and compare observed and calculated net O$_3$ production.

2.5.1 Deviations in O$_3$ production due to clouds and aerosols.

The UH team worked to investigate the impacts of clouds and aerosols on instantaneous O$_3$ production rates during the SHARP 2009 project. To accomplish this, modeled cloud and aerosol free actinic fluxes and photolysis rates were calculated using the 8-stream Tropospheric Ultraviolet and Visible (TUV) version 4.1 radiative transfer model. These cloud free modeled (CFM) rates were used as alternates to the measured photolysis rates from the scanning actinic flux spectroradiometer (SAFS) in the NASA Langley Research Center (LaRC) 0-D box model. Ozone production and loss rates were calculated using the LaRC photochemical box model. To assess the impacts of changes in actinic flux on ozone production and loss rates, the LaRC model was run with photolysis rates from both measured (SAFS) and modeled (CFM) actinic fluxes. The data used in the LaRC model was limited by the availability of concurrent measurements of O$_3$, NO$_2$, HNO$_3$, PAN, VOCs, HCHO, H$_2$O$_2$, and HONO. The design of the LaRC box model is also limited to daytime when $j$(NO$_2$) measurements are available. The results below represent approximately 150 hours of measurements that were able to be modeled.

Figure 2-10 shows two different days during the same season. The left half of the figure shows measured $j$(NO$_2$) in green and calculated net O$_3$ production rates using measured (SAFS) and modeled (CFM) photolysis rates. The upper left shows measured ambient O$_3$ levels and an overcast whole-sky image from around noon. The right half of the figure shows the same data from a few days later with clear skies. The differences in the two O$_3$ production rates on the left are due to the reduction in $j$(NO$_2$) due to the clouds. With very clear skies and light aerosol loadings on the second day, the differences between the CFM and SAFS $j$(NO$_2$) are minimal, resulting in nearly identical O$_3$ production rates. This illustrates how changes in actinic flux affect O$_3$ production. The subsequent analyses will quantify the impacts of clouds and aerosols on $j$(NO$_2$) and O$_3$ production during the SHARP campaign.

![Figure 2-10. Measured O$_3$ and j(NO$_2$), and instantaneous net P(O$_3$) with measured and modeled j(NO$_2$) for a low and high O$_3$ day.](image)

The reduction in measured photolysis rates relative to modeled rates are quantified by taking the ratio of SAFS derived photolysis rates to the CFM rates generated by TUV. This ratio is referred to as the j-value impact factor (JIF), where a 50% reduction in the measured $j(\text{NO}_2)$ compared to modeled $j(\text{NO}_2)$ would have a JIF of 0.5. The median JIF for six cloud free days was 0.98, while the median JIF for the remaining 42 days was 0.83 (Figure 2-11). It should be noted that days designated as cloudy include partly cloudy days which had some periods of clouds and clear skies. There were also two days near the beginning of the project with heavy overcast and rain that strongly reduced $j(\text{NO}_2)$ resulting in JIFs near zero. Figure 2-12 shows two different modes for changes in net O₃ production with JIF. For JIFs of 0.9±0.15, O₃ production can reach instantaneous rates greater than 30 ppbv/hour; however, below JIFs of 0.75 O₃ production decreases linearly with JIF under all conditions.

Figure 2-11. Histogram of $j(\text{NO}_2)$ JIF during SHARP for six cloud free days and 42 days with cloud impacts.
With a 40% reduction in $j(\text{NO}_2)$ (JIF of 0.6), O$_3$ production rates were capped at a maximum at 10 ppbv/hour (Figure 2-12). While other factors besides $j$-values were also regulating ozone production during SHARP (wind speed & direction, boundary layer height, emissions, etc.), reductions in $j(\text{NO}_2)$ correspond to reduced net O$_3$ production rates with a nearly one-to-one relationship, albeit of much smaller net O$_3$ production rates below JIFs of 0.75.

The ratio between calculated ozone production rates with measured (SAFS) and cloud free (CFM) photolysis frequencies (Figure 2-13) highlights the importance of having good photolysis frequency measurements. This linear relationship with a slope near 1 shows that a 20% error in a photolysis rates will result in a 20% error in calculated ozone production. Cloud or aerosol reductions in UV radiation need to be properly accounted for in photochemical model simulations.

Figure 2-12. Peak net P(O$_3$) occurs at JIFs of $\sim$0.75 or greater. Below JIFs of 0.75 net P(O$_3$) decreases with JIF.

Figure 2-13. Net P(O$_3$) varies nearly 1:1 with reductions in $j(\text{NO}_2)$.
Figure 2-14. Average O₃ formation rates for all days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂).

For all conditions, the O₃ destruction terms are nearly an order of magnitude smaller than the formation rates (Figure 2-14). Overall, the impact of clouds and aerosols was to reduce the net O₃ production during the SHARP campaign by an average of ~33% (~2.9 out of 8.9 ppbv/hour).

Several days during the campaign were selected for further examination based on peak 8-hour O₃ and data availability. Four high O₃ days were selected from days with a peak 8-hour O₃ value of 65 ppbv or greater (May 4, 19, 26, and 29th) and four low O₃ days had peak 8-hour O₃ of 40 ppbv or less (May 5, 7, 10, and 17th). For these selected days the O₃ production and loss terms are examined more closely below.

As mentioned previously days with high ozone and high ozone production rates tend to be cloud free. On high ozone days (Figure 2-15) there was approximately a 22% reduction in ozone production (average of 2.4 out of 11.1 ppbv ozone per hour) which was primarily due to aerosol reductions in solar UV radiation. Low O₃ days (Figure 2-16) show a larger reduction in net O₃ production than high O₃ days by nearly a factor of 2, about 40% (3.8 out of 9.6 ppbv/hr) from a reduction in UV radiation due to both clouds and aerosols.
Figure 2-15. Average O3 rates for high O3 days (greater than 65 ppbv for 8-hr average). Darker bars represent calculations with SAFS j(NO2), lighter bars represent calculations with CFM j(NO2).

Figure 2-16. Average O3 rates for low O3 days (less than 40 ppbv for 8-hr average). Darker bars represent calculations with SAFS j(NO2), lighter bars represent calculations with CFM j(NO2).
Figure 2-17. Median diurnal O₃ formation rate for all days and the selected high and low O₃ days. Solid lines represent calculations with CFM j(\text{NO}_2), broken lines represent calculations with SAFS j(\text{NO}_2).

Figure 2-17 shows the median diurnal profile for the O₃ formation rate for all days and the selected high and low O₃ days with solid and broken lines representing the calculated O₃ formation from CFM and SAFS j(\text{NO}_2), respectively. The difference in the CFM O₃ formation on all days and on low days is minimal, however O₃ formation on low days with SAFS j(\text{NO}_2) is significantly reduced compared to the all days profile, especially in the morning and mid-day periods. This would indicate that if it weren’t for the reduction in j(\text{NO}_2) on the low days, which is primarily due to cloud reductions in actinic flux, the peak 8-hour O₃ on those days would likely have been between 40-65 ppbv.

Further examination of the speciated O₃ formation rates on the high and low O₃ days (Figure 2-18 and Figure 2-19) show that under all sky conditions, O₃ formation from HO₂+NO and RO₂+NO are of equal importance and both are affected equally with changes in j(\text{NO}_2).
Figure 2-18. Median diurnal profile of O₃ formation terms for the selected high O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂).

Figure 2-19. Median diurnal profile of O₃ formation terms for the selected low O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂).
The O₃ destruction terms are generally a factor of 6-10 times lower than the formation rates, however, the O₃ destruction rates in Figure 2-20 and Figure 2-21 show that the terms comprising the total destruction rate vary in importance throughout the day, with losses due to NO₂+OH dominating the mornings on both high and low O₃ days. This would tend to indicate that there was an excess of NOₓ which coincides with the morning rush hour observed at the Moody Tower. The relative importance of the other two destruction terms, O¹D+H₂O and O₃+other compounds, also vary in relative importance throughout the day, with O¹D+H₂O following the solar cycle and the photolysis of O₃ to form O¹D, and O₃+other compounds generally following the trend of ambient O₃ levels, low in the mornings and increasing through the day into the afternoon and early evening.

Figure 2-20. Median diurnal profile of O₃ destruction terms for the selected high O₃ days. Darker bars represent calculations with SAFS j(NO₂), lighter bars represent calculations with CFM j(NO₂).
Figure 2-21. Median diurnal profile of O_3 destruction terms for the selected low O_3 days. Darker bars represent calculations with SAFS j(NO_2), lighter bars represent calculations with CFM j(NO_2).

Figure 2-22. Median diurnal O_3 profiles for TRAMP (August & September 2006) and SHARP (April & May 2009). Production rates for CFM and SAFS j(NO_2) are shown in solid and broken lines, respectively.
The peak median O₃ production rates (Figure 2-22) during SHARP occurred during the middle of the day following the diurnal profile of \( j(\text{NO}_2) \) and does not show the strong morning production rates that were found during the TRAMP campaign at the Moody Tower in the late summer of 2006. The overall reductions in O₃ production due to clouds and aerosols during SHARP was \( \sim 2.9 \text{ ppbv/hr} \), compared to \( \sim 8 \text{ ppbv/hr} \) during TRAMP.

Key Findings:

- The impact of clouds and aerosols was to reduce the net O₃ production during the SHARP campaign by an average of \( \sim 33\% \) (\( \sim 2.9 \text{ ppbv/hr} \))
- The peak in the median diurnal net O₃ production profile was \( \sim 16 \text{ ppbv/hr} \)
- The peak median O₃ production rates during SHARP occurred during the middle of the day and does not show the strong morning production rates that were found during TRAMP

2.5.2 Comparison of MOPS measured ozone production rate with model calculations

A time series shows the general behavior of the 10-minute calculated, measured and modeled \( P(O_3) \) and ambient ozone levels during SHARP (Figure 2-23). The measured \( P(O_3) \) obtained using the MOPS shows the expected diurnal variations for \( P(O_3) \), although the peak values vary day to day. The MOPS started measuring on 19 April, 2009 and measured \( P(O_3) \) on 20 days.

In early May, high northward winds, considerably cloudiness, and morning or afternoon showers suppressed ozone production as well as ozone. With the exception of 4 May, \( P(O_3) \) did not exceed 25 ppbv h⁻¹ and ozone did not exceed 50 ppbv. More polluted conditions occurred later in the study. The meteorological conditions on 4, 19, 20 and 21 May were such that high data quality was obtained with the MOPS. The afternoon temperatures peaked at near 30°C and the sky was clear. The wind speed was low in the morning, between 1 m s⁻¹ and 4 m s⁻¹ blowing from the N, NE directions, and the relative humidity ranged between 30 – 50% at noon. These conditions were optimal for ozone formation and accumulation in the air. The Texas Commission on Environmental Quality (2011) reported officially that 4, 20 and 29 May were pollution events. Ambient ozone on these days surpassed 80 ppbv and the peak \( P(O_3) \) measured with the MOPS was higher than 40 ppbv h⁻¹.
Figure 2-23. Time series from 19 April (day 119) to 30 May (day 150), 2009 for ambient ozone (green dots), calculated P(O\textsubscript{3}) from ancillary measurements (black circles), measured P(O\textsubscript{3}) with the MOPS (blue dots) and modeled P(O\textsubscript{3}) from the RACM2 mechanism (red dots).

The dependence of measured P(O\textsubscript{3}) on measured NO evolves over the period from 19 May to 21 May, a period of high pollution (Figure 2-24). Peak P(O\textsubscript{3}) measured with the MOPS reached 60 ppbv h\textsuperscript{-1} on 19 May, a higher value of 75 ppbv h\textsuperscript{-1} on 20 May, and then peaked at a lower value of 40 ppbv h\textsuperscript{-1} on 21 May. These relative P(O\textsubscript{3}) values are consistent with the relative O\textsubscript{3} values for the same days (Figure 2-23).
Figure 2-24. Measured $P(O_3)$ in NO space for the high ozone episode that started on 19 May, developed on 20 May and subsided on 21 May, 2009 in Houston. The color scale corresponds to hour of the day. The number on top of every curve is the date in May.

The plotted data in Figure 2-24 are the 10-minute MOPS data without any smoothing or correction. Reading the plots from right to left, using the hour of the day given by the color scale, it is clear that the curves start with high NO and low $P(O_3)$ before 8:00, grow rapidly as NO falls past the rush hour, reach broad peaks at around 10:00 when NO ranges between 2-10 ppbv, and finally decrease in the afternoon and evening as NO decreases. Note particularly that the peak ozone production occurs at mid to high levels of NO, about 10:00, and that the higher the daily peak $P(O_3)$ was, the more it peaked at higher NO.

A comparison for the entire data sets for the measured, calculated, and modeled $P(O_3)$ as a function of NO are shown in Figure 2-25, but only for times when all three methods are available and only for times between 5:00 and 20:00. Not all measured $P(O_3)$ shown in Figure 2-24 appear in Figure 2-25 because there were no calculated or modeled $P(O_3)$ points for some of the measured $P(O_3)$ points in Figure 2-24 and only overlapping points for all three methods are shown in Figure 2-25.
A first observation from Figure 2-25 has to do with the low modeled P(O₃) values compared to the measurements and the calculations. For the same hour of the day and the same NO levels, the modeled P(O₃) is substantially lower than the measured and calculated P(O₃) suggesting a potential lack of a source of radicals in the model. Moreover, there is rough agreement between the measured and calculated P(O₃) for the magnitude of the peak P(O₃), although the calculated P(O₃) has more high values at higher NO levels. In addition, both the calculated and modeled P(O₃) are close to zero with low scatter for evening hours whereas the MOPS data are more scattered and include negatives, possibly due to the formation of HNO₃ or other artifacts as discussed previously. Thus, while the NO dependence of the MOPS measurement has qualitative similarities with the NO dependence of both the calculated and the modeled P(O₃), its shape is closer to that of the modeled P(O₃) but its magnitude is closer to that of the calculated P(O₃).

Key Findings:

- MOPS measured P(O₃) peaked in the late morning, with values between 15 ppbv h⁻¹ and 100 ppbv h⁻¹, although values of 40–80 ppbv h⁻¹ were typical for higher ozone days
- Measured and calculated P(O₃) had similar peak values but the calculated P(O₃) tended to peak earlier in the morning when NO values were higher
- Measured and modeled P(O₃) had a similar dependence on NO, but the modeled P(O₃) was only half the measured P(O₃)
- These differences indicate possible missing radical sources in the box model with the RACM2 mechanism and thus has implications for the ability of air quality models to accurately predict ozone production rates
Objective 6. Study the sensitivity of \( \text{O}_3 \) production to \( \text{NO}_x \) and VOCs.

VOC-\( \text{NO}_x \)-\( \text{O}_3 \) chemistry has been studied for decades. However, the oxidation pathways are complex and most studies have been done in large environmental chambers with high \( \text{NO}_x \) levels. As a result, even though the basic reaction pathways appear to be understood, much of the detailed chemistry remains unresolved. One of the most important consequences of this chemistry is the production of pollutants, particularly ozone. Thus, the ozone production rate is literally the production rate of \( \text{NO}_2 \) molecules from \( \text{HO}_2 + \text{NO} \) and \( \text{RO}_2 + \text{NO} \) reactions. The calculated instantaneous ozone production rate \( P(\text{O}_3) \) can be written as the equation:

\[
P(\text{O}_3) = \left( k_{\text{HO}_2+\text{NO}}|\text{HO}_2| + \sum_i k_{\text{RO}_2+\text{NO}}|\text{RO}_2| \right) |\text{NO}|
\]

where \( k_{\text{HO}_2+\text{NO}} \) and \( k_{\text{RO}_2+\text{NO}} \) are the reaction rate coefficients for reactions of \( \text{HO}_2 \) and \( \text{RO}_2 \) with \( \text{NO} \). At low \( \text{NO} \) conditions (\( \text{NO}_x \)-sensitive), VOCs are more competitive than \( \text{NO}_x \) for reacting with OH so that radical–radical reactions dominate \( \text{HO}_x \) chemistry. The produced peroxy radicals can then convert \( \text{NO} \) to \( \text{NO}_2 \). Every \( \text{NO}_2 \) molecule that is generated from this reaction sequence will make an \( \text{O}_3 \) molecule. So OH mainly reacts with VOCs, makes more radicals, and potentially increases \( \text{O}_3 \) in the presence of \( \text{NO} \). In the high \( \text{NO}_x \) condition (VOC-sensitive), the OH reaction with \( \text{NO}_2 \) should reduce the ozone production because \( \text{HO}_2 \) reacts with \( \text{NO} \) to form more OH, which then is terminated by the reaction with \( \text{NO}_2 \).

Kleinman (2005) introduces a formula to evaluate the \( \text{O}_3 \) production sensitivity using the ratio of \( L_\infty/Q \), where \( L_\infty \) is the radical loss via the reactions with \( \text{NO}_x \) and \( Q \) is the total primary radical production. Because the radical production rate is equal to the radical loss rate, this ratio represents the fraction of radical loss due to \( \text{NO}_x \). When \( L_\infty/Q < 0.5 \), the atmosphere is in the \( \text{NO}_x \)-sensitive region, and when \( L_\infty/Q > 0.5 \), the atmosphere is in the VOC-sensitive region.

The ozone production sensitivity to \( \text{NO}_x \) or VOCs has a similar behavior for TexAQS 2000, TRAMP 2006 (Mao et al., 2010) and SHARP 2009; it is VOC sensitive in the early morning and late afternoon but \( \text{NO}_x \)-sensitive throughout the afternoon (Figure 2-26). This behavior is typical of US urban areas. These results are independent of the differences between the measured and modeled OH and \( \text{HO}_2 \). Note that in the afternoon the ozone sensitivity in SHARP 2009 has a longer \( \text{NO}_x \)-sensitive period than TexAQS 2000 and TRAMP 2006, indicating that \( \text{NO}_x \) control is an efficient approach for the \( \text{O}_3 \) control in spring time.
Figure 2-26. Median diurnal profiles of $L_N/Q$ in TEXAQS 2000, TRAMP 2006, and SHARP 2009.

Key Findings:

- The ozone production sensitivity to NO$_x$ or VOCs in Houston had a similar behavior in TexAQS 2000, TRAMP 2006, and SHARP 2009 (VOC sensitive in the early morning and late afternoon but NO$_x$ sensitive throughout the afternoon) and is typical of US urban areas.
- Afternoon the ozone sensitivity in SHARP 2009 has a longer NO$_x$-sensitive period than TexAQS 2000 and TRAMP 2006, indicating that NO$_x$ control is an efficient approach for the O$_3$ control in spring time.
2.6 Objective 7. Investigate the potential of HONO as a daytime precursor of OH.

2.6.1 Objective 7A. Importance of HONO in HOx budget

A number of previous studies have found that there are significant daytime HONO levels existing in urban environments which can be photolyzed to produce OH radicals and thus contribute to daytime HOx production. We looked at HOx budget during SHARP. The total HOx production includes the following processes: the ozone photolysis followed by the reaction of O(1D) with H2O, the HONO photolysis, the HCHO photolysis (the radical-produced pathway), and the O3 reactions with alkenes. HOx loss includes the processes: the OH reaction with NO2, and the reactions between OH, HO2 and RO2. Calculated HOx production is dominated by photolysis of HONO in the early morning and by O3 photolysis in the midday (Figure 2-27), and is mainly from O3 reactions with alkenes a night. On average, the daily HOx production rate was 23.8 ppbv day⁻¹, of which 31% is from O3 photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O3 reactions with alkenes. For HOx loss, the clearly dominant process was the OH reaction with NO2, while the self-reactions between OH, HO2, RO2 become important in the afternoon when their concentrations reach the highest.

Figure 2-27. Diurnal variation of HOx production (top) and HOx loss (bottom). HOx production processes include ozone photolysis followed by the O1D + H2O reaction, the photolysis of HONO, the photolysis of HCHO, and ozone reactions the alkenes. HOx loss
processes include OH reaction with NOx, HO2+HO2 reaction and HO2 + RO2 reactions. RACM2 modeled results are used.

Key Findings:
- Calculated HOx production was dominated by HONO photolysis in the early morning and O3 photolysis in the midday. At night OH production was mainly from O3 reactions with alkenes.
- On average, the daily HOx production rate was 23.8 ppbv day\(^{-1}\) (31% from O3 photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O3 reactions with alkenes)
- HOx loss was dominated by OH + NO2, while the self-reactions between OH, HO2, RO2 become important in the afternoon

2.6.2 1-D Box Modeling of daytime HONO

To further understand daytime HONO formation in Houston during SHARP we analyzed UCLA’s long path-DOAS observations of vertical concentration profiles of HONO, NO2, and other species (see Wong et al, 2011 for a more thorough description). Figure 2-28 shows the observations of HONO, NO2, and other parameters made by the collaborators in this project on a sunny day during the 2009 SHARP experiment in Houston. Early morning HONO mixing ratios generally followed those of NO2, showing distinct vertical gradients, with larger mixing ratios near the ground than aloft, and decreased from ~0.3 ppb at sunrise to ~0.15 ppb at 9:00 CST. Throughout the rest of the day, HONO mixing ratios in all three height intervals remained between 0.05 to 0.15 ppb. Generally, HONO mixing ratios decreased slightly throughout the day, in contrast to NO2, which increased after noon. Using Equation 2 with the measured NO and \(J_{HONO}\), and the average OH data on sunny days during SHARP observations, it was possible to calculate the HONO steady-state mixing ratio. Steady-state HONO mixing ratios were about 0.02 ppb in the late morning and decreased to 0.01 ppb in the afternoon. The elevated daytime HONO concentrations indicated a strong unknown source of HONO during the day. HONO mixing ratios also showed statistically significant vertical gradients throughout the day, with smaller mixing ratios in the upper height interval than in the lower and middle intervals.

\[
[HONO]_{ss} = \frac{k_{NO+OH}[NO][OH]}{J_{HONO} + k_{OH+HONO}[OH]} \tag{2}
\]
Figure 2-28. Timeseries of meteorological data, $J_{\text{NO}_2}$, NO, OH, HONO, NO$_2$ and HONO to NO$_2$ ratio on April 21, 2009. LP-DOAS HONO, NO$_2$, and HONO/NO$_2$ data are color codes by altitude interval: lower 20-70m, middle: 70-130m, and upper: 130-300m. HONO and NO$_2$ data after 9:00 CST are displayed with different scales on the right y-axis. Error bars of one standard deviation are shown on NO$_2$, HONO and HONO/NO$_2$. Please note that the OH data shown here is the average of OH observed during sunny days in Houston.
To understand this unknown source of HONO we used a pseudo steady state approach (Equations 3 and 4) to further analyze the HONO formation rate, $P_{\text{unknown}}$.

$$P_{\text{unknown}} + k_{\text{NO} + \text{OH}[\text{NO}][\text{OH}]} - J_{\text{HONO}}[\text{HONO}] - k_{\text{OH} + \text{HONO}}[\text{HONO}][\text{OH}] + E = 0$$ (3)

$$P_{\text{unknown}} = J_{\text{HONO}}[\text{HONO}] + k_{\text{OH} + \text{HONO}}[\text{HONO}][\text{OH}] - k_{\text{OH} + \text{NO}}[\text{NO}][\text{OH}] - E$$ (4)

Figure 2-29 shows the result of this calculation for two days during SHARP compared to other known daytime HONO sources. It is obvious that the unknown HONO source dominates throughout both days. $P_{\text{unknown}}$ shows a clear diurnal variation with somewhat higher HONO formation rates in the morning. This asymmetry can be explained by the dependence of $P_{\text{unknown}}$ on NO$_2$, or another gas that is well correlated with NO$_2$.

Figure 2-29. Time series of HONO formation and removal rates at the lower height interval on April 21, 2009 (left) and May 18, 2009 (right). Please note that errors were propagated from the statistical uncertainties in the observations.

To remove the NO$_2$ dependence we divided $P_{\text{unknown}}$ by the NO$_2$ concentration. This NO$_2$-normalized HONO formation rate, $P_{\text{norm}}$, is shown in Figure 2-30. $P_{\text{norm}}$ is now symmetric around noon and correlated to the actinic flux and solar irradiance.

Figure 2-30. Time series of $P_{\text{norm}}$ in the lower and middle height intervals on April 21, 2009 (left) and May 18, 2009 (right). $P_{\text{norm}}$ in the upper height intervals was not calculated due to insufficient data. Photolysis frequency of NO$_2$ and solar irradiance are shown as well for comparison.
The observations of diurnal variations of $P_{\text{unknown}}$ and $P_{\text{norm}}$ together with the HONO vertical gradients, allow a number of different interpretations of the possible HONO sources:

Source 1) HONO is formed by a photolytic gas-phase source that either involves NO$_2$ or that is based on a precursor that shows a similar vertical and temporal profile as NO$_2$, assuming that the actinic flux does not significantly change with altitude.

We found no evidence for a gas-phase HONO formation based on the analysis of the expected diurnal profile $P_{\text{norm}}$, which would show a minimum at noon for the NO$_2$$\rightarrow$NO$_2^*$ pathway and would not be well correlated with solar radiation in the case of the nitrophenol photolysis pathway.

Source 2) HONO is formed by photolytically enhanced conversion of NO$_2$ on the aerosol. If the aerosol profile is fairly uniform in the lowest 300m of the atmosphere, and one assumes that actinic flux does not change, HONO would reach a steady state with NO$_2$ at all altitudes, i.e. HONO/NO$_2$ would not show a gradient.

This formation pathway would predominately depend on aerosol surface area concentration and actinic flux. If it proceeds through nitrate photolysis a dependence on aerosol nitrate would also be expected. However NO$_2$ and aerosol nitrate measured during SHARP are not closely correlated and we thus believe that the nitrate photolysis pathway is not important. To explain our observations (Figure 2-28, Figure 2-29, and Figure 2-30) the aerosol surface area concentration would also have to fairly constant throughout the day, which was not observed during SHARP. The final piece of evidence against an aerosol mediated NO$_2$ to HONO conversion is the dependence on actinic flux vs. solar irradiance. In the case of an aerosol formation pathway one would expect that $P_{\text{norm}}$ is better correlated with the actinic flux than with solar irradiance. We thus performed a correlation analysis for four sunny day during SHARP (Figure 2-31). This analysis shows a better correlation of $P_{\text{norm}}$ with solar irradiance than with actinic flux (Table 2-3), strongly pointing to a NO$_2$ to HONO conversion on the ground, rather than the aerosol. We thus concluded that daytime conversion of NO$_2$ to HONO on the aerosol is not important in Houston.

Source 3) HONO is formed on the ground by a photolytically enhanced conversion of NO$_2$, and then transported upwards.

Following the arguments against an aerosol formation pathway we concluded that the most likely source of daytime HONO is a photocatalytic conversion of NO$_2$ on the ground. This conversion is proportional to solar irradiance, where we cannot clearly distinguish whether UV or visible wavelength ranges are more important (Table 2-3), and the NO$_2$ concentration. As Table 2-3 shows the slope between $P_{\text{norm}}$ and solar irradiance are quite similar on all days and we believe that we may be able to use this parameterization in atmospheric chemistry models for the Houston area. The parameterization of HONO formation in the lower 300m of the Houston atmosphere would look as follows:

$$P_{\text{HONO}}=3.3 \times 10^{-8} \text{ m}^2 \text{ W}^{-1} \text{ s}^{-1} \times (\text{visible solar irradiance}) \times [\text{NO}_2]$$ (5)
Figure 2-31. Correlations between $P_{\text{norm}}$ and $J_{\text{NO2}}$ (panel a) and solar visible irradiance (panel b) at lower and middle height intervals on four sunny days (April 21, May 4, May 18 and May 19) during SHARP 2006. Results of the linear fits are shown in Table 2-3.

<table>
<thead>
<tr>
<th>Date</th>
<th>Lightpath</th>
<th>$J_{\text{NO2}}$</th>
<th>solar visible irradiance</th>
<th>solar UV irradiance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope ($10^{-3}$)</td>
<td>$R^2$</td>
<td>Slope ($10^{-4}$ m$^2$W$^{-1}$s$^{-1}$)</td>
</tr>
<tr>
<td>4/21</td>
<td>lower</td>
<td>2.7±0.3</td>
<td>0.64</td>
<td>3.1±0.2</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>4.2±0.3</td>
<td>0.76</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td>5/4</td>
<td>lower</td>
<td>3.9±0.2</td>
<td>0.92</td>
<td>3.6±0.1</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>3.9±0.2</td>
<td>0.93</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td>5/18</td>
<td>lower</td>
<td>3.2±0.2</td>
<td>0.84</td>
<td>3.2±0.2</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>3.4±0.2</td>
<td>0.91</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td>5/19</td>
<td>lower</td>
<td>3.9±0.4</td>
<td>0.83</td>
<td>3.6±0.3</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>3.7±0.5</td>
<td>0.73</td>
<td>3.5±0.4</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>3.6±0.3</td>
<td>0.82</td>
<td>3.5±0.2</td>
</tr>
</tbody>
</table>

Table 2-3. Linear fits results of Figure 2-31.

We also used the LP-DOAS observations together with the actinic flux measurements to study the altitude dependence of primary OH formation in Houston. We compared the OH formation rate from the photolysis of ozone to O'\text{D}, followed by its reaction with water, the photolysis of HCHO, assuming that the formed HO$_2$ instantly reacts with NO, and the photolysis of HONO. Above it was showed that the reaction of OH + NO is unimportant as a source of HONO, and thus we did not correct the OH formation from HONO photolysis by the rate of this back-reaction. The calculations were based on UCLA’s LP-DOAS observations of O$_3$, HCHO, and HONO, as well as actinic flux and meteorological measurements by the Univ. of Houston.

Figure 2-32 shows the results of this calculation for three sunny days in Houston. The days are the same than those discussed previously. Shown are the three formation pathways in three altitude intervals: 20-70m (low), 70-130m (middle) and 130-300m (up). In general, HONO photolysis dominates in the lowest and middle light path in the morning. Morning HONO
photolysis in the upper height interval is about equally important as HCHO, and sometimes $O_3$, photolysis. At around 10:00 CST ozone photolysis becomes the most important OH source.
Figure 2-32. OH production rates on three sunny days in Houston during the SHARP 2009 experiment. Shows are the rates in three different height intervals: low (20-70m), (mid) 70-130m and (up) 130-300m.

However, both HCHO and HONO photolysis remain important. It is interesting to note that OH formation from ozone and HCHO photolysis show little altitude dependence, although it appears that O₃ photolysis is slightly higher aloft. In contrast, OH formation through HONO photolysis shows very distinct gradients, with higher rates near the surface. In the lower two height intervals HONO photolysis is the second most important OH source after 10:00 CST. In the upper interval HCHO photolysis is equally or even more important than HONO photolysis. It should be noted that in the later afternoon HONO photolysis again becomes the dominant OH source in the lowest two height intervals. It will be interesting to compare these results with those from our 1D model and urban air quality models to see if the observed behavior is reproduced by the models.

1-D Chemistry and transport model simulations were carried out to validate the results of our observational analysis which showed that daytime HONO mixing ratios were due to photoenhanced conversion of NO₂ into HONO at the ground. Five set of model runs with different daytime HONO formation pathways were performed. These include model runs (1) without a photolytic HONO source, (2) with photolytic HONO formation at the ground only, (3) on aerosol only, (4) in the gas-phase only, and (5) both at the ground and on aerosol (see Figure 2-33). Photolytic HONO formation at the ground and on aerosol was parameterized by a function in which the reactive NO₂ uptake coefficient at the ground depends on solar irradiance and NO₂ photolysis frequency respectively. For the model run with photolytic gas-phase HONO formation, the chemical reactions which lead to the reaction of photoexcited NO₂ with water vapor were implemented in the model.

Model run #1) No photolytic HONO source was considered.
Model significantly underestimated HONO mixing ratios at all three height intervals as well as the [HONO]/[NO₂] ratios.

Model run #2) Photolytic ground source of HONO was included at the ground only.
Modeled HONO mixing ratios in the lower height intervals agreed much better with the observations. The modeled HONO mixing ratios in the lower height intervals were within ±20% of the observations and often within the errors of the observations. However, the modeled HONO mixing ratios in the middle and upper height intervals were still smaller than the observations. The modeled [HONO]/[NO₂] ratios showed much better agreement with the observed ratios. Although the modeled [HONO]/[NO₂] ratios showed a clear diurnal variation, consistent vertical gradients which were not observed were calculated by the model. In general, the ratio in the lowest height intervals showed good agreement with the observations while the ratios in the middle and upper height intervals were under-predicted by the model. The underestimated HONO mixing ratios in the middle and upper height intervals in the model suggested that in addition to the ground source, a HONO source occurring either on aerosol or in the gas-phase was also present.

Model runs #3 and #4) Photolytic HONO formation was considered on aerosol only and in gas-phase only.
Both sets of model simulations showed very similar model results in the HONO mixing ratios and [HONO]/[NO₂] ratios. Both model runs showed HONO mixing ratios of within ±20% of the observations at all height intervals, except that the morning peaks were overestimated in the lower and/or middle height intervals. Despite the decent HONO model results, the modeled [HONO]/[NO₂] ratios were almost constant.
throughout the day, in contrast to the observations that showed a clear diurnal variation. The disagreement of the [HONO]/[NO₂] ratios between the model and the observations indicated that aerosol and gas-phase formation cannot be the dominant source of daytime HONO.

Model run #5) Photolytic HONO formation was included predominately at the ground and to a lesser extent on aerosol.

The best agreements of HONO and [HONO]/[NO₂] ratios between the model and observations were achieved when photolytic HONO formation was considered both at the ground and on aerosol. HONO mixing ratios in the middle and upper height intervals were in general within ±15% of the observations. Although the modeled [HONO]/[NO₂] ratios showed better agreement with the observations, there were still consistent vertical gradients in the ratios which were not observed. The vertical gradients in the ratios were partially due to the overestimated NO₂ mixing ratios in upper height intervals in the model. If the NO₂ mixing ratios in the upper height intervals were perfectly simulated, the ratio [HONO]/[NO₂] ratios in the upper height intervals would be similar to that in the middle height intervals. It was thus possible that the cause of the [HONO]/[NO₂] profile in the model were an inaccurate modeling of NO₂ and its vertical distribution. It should also be noted that the errors of [HONO]/[NO₂] ratio were quite large and that it might be possible that the complete lack of a [HONO]/[NO₂] gradient in the observations was not statistically significant.

Model calculations were performed for two sunny days (May 18 and May 19, 2009) during SHARP. All model simulations of daytime HONO were consistent with the results of our observational analysis which indicated that daytime HONO observations were mainly caused by photoenhanced NO₂ conversion into HONO at the ground and to a smaller degree on aerosol.

![Figure 2-33. Comparisons of daytime HONO, NO₂ and [HONO]/[NO₂] ratios between observations and different model simulations on April 21, 2009.](image-url)
Key Findings:

- Steady-state HONO mixing ratios were about 0.02 ppb in the late morning and decreased to 0.01 ppb in the afternoon indicating a strong unknown source of HONO during the day.
- Significant vertical gradients exist throughout the day, with smaller mixing ratios aloft.
- The most likely source of daytime HONO is a photocatalytic conversion of NO$_2$ on the ground proportional to solar irradiance.
- The following general parameterization of HONO formation in the lower 300m of the Houston atmosphere was developed: $P_{\text{HONO}} = 3.3 \times 10^{-8} \text{ m}^2\text{W}^{-1}\text{s}^{-1} \times \text{(visible solar irradiance)} \times [\text{NO}_2]$.
2.7 Objective 8. Evaluate the role of ClNO\textsubscript{2} as an early morning radical source and its contribution to ozone production.

The importance of ClNO\textsubscript{2} as an early morning radical source and its contribution to ozone production is evaluated in the RACM2 mechanism by including chlorine chemistry in RACM2. The chlorine chemistry was mainly adopted from the NASA JPL 2010 evaluation (Sander et al., 2011), including 54 inorganic reaction, 13 photolysis reactions of chlorine species, 32 Cl reactions with VOCs, and reactions among organic peroxy radicals (RO\textsubscript{2}) initiated by Cl. Besides the standard RACM2 constraints, the revised RACM2 model was additionally constrained by the measured ClNO\textsubscript{2} and HCl to calculate Cl and Cl-initiated peroxy radicals. We found that without additional chlorine sources in the model (base run), the modeled organic peroxy radicals initiated by Cl is less than 1% of those initiated by OH and O\textsubscript{3} (Figure 2-34). The modeled concentrations of Cl and Cl\textsubscript{2} are too low compared to some previous observations (e.g., Riemer et al., 2008; Finley and Saltzman, 2006). Apparently additional chlorine sources are needed in the model in order for the Cl chemistry to be important in photochemistry and ozone production.

![Figure 2-34. Model results in a base run with RACM2 plus chlorine chemistry. The model was constrained by measured ClNO\textsubscript{2} and HCl without additional Cl sources.](image)

Two sensitivity runs were performed: one with the model constrained by a constant [Cl\textsubscript{2}] of 20 pptv and the other with the model constrained by a constant [Cl\textsubscript{2}] of 100 pptv. Results from these two sensitivity runs are shown in Figure 2-35 and Figure 2-36. When the model includes a constant [Cl\textsubscript{2}] of 20pptv, the modeled RO\textsubscript{2} concentration initiated by Cl is up to 7% of that initiated by OH and Cl concentration is on the order of 10\textsuperscript{4} molecules cm\textsuperscript{-3}. In the second sensitivity run when the model includes a constant [Cl\textsubscript{2}] of 100pptv, the modeled RO\textsubscript{2} concentration initiated by Cl is up to 28% of that initiated by OH and Cl concentration is on the order of 10\textsuperscript{5} molecules cm\textsuperscript{-3}. The modeled Cl concentrations in these two sensitivity runs are comparable to the derived Cl concentrations from isoprene+Cl oxidation products during TexAQS2000 (Riemer et al., 2008), suggesting that Cl chemistry may be important in oxidation chemistry and ozone production if there is sufficient chlorine sources.
Figure 2-35. Model results in a sensitivity run with RACM2 plus chlorine chemistry. The model was constrained by measured ClNO₂ and HCl and a constant [Cl₂] of 20 pptv.

Figure 2-36. Model results in a sensitivity run with RACM2 plus chlorine chemistry. The model was constrained by measured ClNO₂ and HCl and a constant [Cl₂] of 100 pptv.

Key Findings:
- Without additional chlorine sources in the model, modeled organic peroxy radicals initiated by Cl is less than 1% of those initiated by OH and O₃
- Modeled concentrations of Cl and Cl₂ are too low compared to previous observations, indicating that additional chlorine sources are needed in the model in order for the Cl chemistry to be important in photochemistry and ozone production.
- Cl chemistry may be important in oxidation chemistry and ozone production if there are sufficient chlorine sources, however additional measurements of chlorine species are needed to assess the potential role of halogen chemistry in the Houston atmosphere
2.8 Objective 9. Correlations between HNO₃ and gas phase chloride, and their implications for coupled Cl and NOx chemistry in Houston.

Gaseous nitric acid (HNO₃) and gas phase soluble chloride (Cl⁻) were highly correlated on short (minutes to hours) time scales throughout the SHARP campaign (Figure 2-37). This correlation between soluble Cl⁻ and HNO₃ was discovered during the early days of SHARP campaign and re-analysis of the 2006 TRAMP data revealed that this phenomenon also occurred during that project. Peak mixing ratios of soluble Cl⁻ (Figure 2-38) occurred during transport from south (i.e., clean conditions) with lower mixing ratios occurring in polluted from the north and east (Figure 2-38). Overall the opposite conditions resulted in peak HNO₃ mixing ratios (Figure 2-38 and Figure 2-39) yet there is a remarkably strong correlation between HNO₃ and soluble Cl⁻ from sample to sample and diurnally (Figure 2-40) were observed regardless of wind direction (Figure 2-41).

It should be noted that the mixing ratios of soluble Cl⁻ are substantial in Houston. Even during intervals with sustained northerly flow (relatively low Cl⁻) daytime maxima routinely exceeded 1 ppbv. Similar observations made during TexAQS 2006 on the Moody Tower and the NOAA vessel Ronald H. Brown indicate that abundant soluble Cl⁻, linked with HNO₃ by processes not yet understood, is characteristic of the Houston-Galveston Bay region during both spring and summer.

![Figure 2-37. Time series of soluble chloride gas (which is thought to be gaseous HCl) and HNO₃ during SHARP campaign.](image-url)
Figure 2-38. Time series of soluble chloride gas (which is thought to be gaseous HCl) and HNO₃ during SHARP campaign during a relatively clean period (April 24-26th 2009) during period of southerly air flow. Note the higher ratio between gaseous chloride and HNO₃ and striking covariation in daytime.
Figure 2-39. Time series of soluble chloride gas and HNO$_3$ during SHARP campaign during a relatively polluted period (May 29-30th 2009) during period of northerly air flow. Note the lower ratio between gaseous chloride and HNO$_3$ and the very large differences in scaling between Figure 2-38 and Figure 2-39. Yet chloride and nitric acid still have very strong covariance.
Figure 2-40. Hourly mean diurnal mixing ratios of HNO₃ (top) and soluble Cl⁻ (bottom) during SHARP. Nighttime enhancements of HNO₃, but not soluble Cl⁻ occurred fairly frequent during SHARP. This suggests an alternative HNO₃ production pathway, perhaps through N₂O₅.
Study of Houston Atmospheric Radical Precursors (SHARP) Data Analysis
AQR Project 10-032

Figure 2-41. Relative abundance of soluble gaseous Cl\textsuperscript{-} compared to HNO\textsubscript{3} during SHARP of all days (top). Same ratio plotted as a function of wind direction. Note large increase in soluble gaseous Cl\textsuperscript{-} during southerly flow.

Key Findings:
- Correlations between gaseous HNO\textsubscript{3} and gas phase chloride were highly correlated on short time scales throughout the SHARP & TRAMP campaigns
- Peak mixing ratios of soluble gaseous Cl\textsuperscript{-} occurred during transport from south with lower mixing ratios occurring in polluted air from the north and east, while HNO\textsubscript{3} showed the opposite behavior
- During intervals with sustained northerly flow (relatively low Cl\textsuperscript{-}) daytime soluble Cl\textsuperscript{-} routinely exceeded 1 ppbv, and was similar to observations made during TexAQS 2006 on the Moody Tower and the NOAA vessel Ronald H. Brown, indicating that abundant soluble Cl\textsuperscript{-}, linked with HNO\textsubscript{3} by processes not yet understood, is characteristic of the Houston-Galveston Bay region during both spring and summer
3. PROJECT SUMMARY

The following is a summary of the primary conclusions from our data analysis of the SHARP campaign in Houston during the Spring of 2009:

On way of evaluating our understanding of photochemistry and confidence in using photochemical models to inform policy is to examine how photochemical box models replicate the measured OH and HO$_2$ levels. All the various photochemical box models tested in this study exhibit similar diurnal and day-to-day variations, with maxima in the early afternoon and minima at night. In general, the models reproduced the observed OH and HO$_2$ with all 5 chemical mechanisms (RACM2, CB05, LaRC, SAPRC07, and MCMv3.1) producing similar levels of OH and HO$_2$. Notably CB05 produced slightly higher HO$_2$ than measured and significantly less OH than the others. Given that HO$_2$ is approximately 20 times higher than OH during the day, the CB05 model predicted the closest total HO$_x$ of all five mechanisms. The most significant differences between the measurements and modeled HO$_x$ was that the models on average overpredicted daytime OH by approximately 23% and nighttime HO$_2$ was underpredicted by approximately 49%. The differences among the 5 mechanisms are mainly due to the different treatments of VOCs, i.e., MCM has an explicit VOC reaction scheme, while all other 4 mechanisms have lumped VOC species with different functional groups. This is an encouraging result suggesting that not much modeling skill has been lost by employing lumped VOC reaction schemes in the regional chemical transport models used for SIP evaluations.

The observed-to-modeled OH and HO$_2$ ratios can test our understanding of the HO$_x$ photochemistry because the cycling between OH and HO$_2$ is very fast and the photochemical equilibrium among OH and HO$_2$ is closely tied to the interconversion of NO and NO$_2$ in the troposphere. Similarly, VOCs also play a critical role in HO$_x$ chemistry as VOCs react with OH to act as OH sinks and to produce organic peroxy radicals, RO$_2$. Using the average model results from the five mechanisms, the predicted OH agrees well with measurements at moderate NO levels (between a few hundred pptv and a few ppbv) but underpredicts OH at both lower and higher NO levels. The observed-to-modeled ratio for HO$_2$ is fairly constant around 2, however the measurement/model agreement significantly deteriorates (i.e., models significantly under predict HO$_2$) at “high” NO mixing ratios (greater than 3 ppbv).

An evaluation of the OH reactivity helps determine if the suite of measured compounds are sufficient to capture the total in situ measured OH reactivity. While instrumental problems limited the availability of OH reactivity measurements, the calculated OH reactivity from measured species account for about 94% of the total calculated OH reactivity. This result indicates that modeled organic intermediates do not contribute significantly to the OH reactivity, in other words, there does not appear to have been any appreciable “missing” OH reactivity, in contrast with the Fall 2006 TRAMP campaign.

At night two different pathways can contribute to HO$_x$ production: (1) O$_3$ reactions with alkenes to make HO$_x$, and (2) NO$_3$ reactions with VOCs such as HCHO, unsaturated aldehydes, methacrolein, and glyxal to produce HO$_x$. This analysis found that during SHARP, NO$_3$ chemistry contributes less HO$_x$ production than the O$_3$ + alkene reaction with the exception of 5 nights where O$_3$ levels were greater than NO, leaving residual O$_3$ for NO$_3$ production. Nighttime HO$_2$ production from O$_3$+alkene reactions contributes about 68% of the total, with the remainder coming from NO$_3$ chemistry. Measurements made by long path DOAS during SHARP indicate that there is significant NO$_3$ formation at higher altitudes where lower nighttime NO levels are observed.
The measured OH concentrations in Houston during SHARP are comparable to the OH measurements in other cities (Mexico City, Nashville, New York). However, the peak HO2 concentrations are significantly higher in Mexico City, partly due to the much higher VOC levels as compared to the other cities. HO2 concentrations in New York City are unusually low because of the high NOx concentrations throughout the day. Springtime HO2 levels in Houston are more or less like those in Nashville. The similarity of OH levels in these cities indicates that the OH production and loss rate are well buffered in urban environments.

The quality of ozone modeling depends on many factors, including correctly accounting for the radiative effects of clouds and aerosols on photolysis frequencies. UV actinic flux is reduced throughout the troposphere by clouds and aerosols, leading to a reduction in near-surface ozone production. Overall, the impact of clouds and aerosols was to reduce the net O3 production during the SHARP campaign by an average of ~33% (~2.9 out of 8.9 ppbv/hour). Days with high ozone (and high ozone production rates) tended to be cloud free, consequently the calculated 22% reduction in ozone production was primarily due to aerosol reductions in solar UV radiation. Low O3 days showed a larger reduction (~40%) in net O3 production than high O3 days due to a reduction in UV radiation by both clouds and aerosols. The O3 destruction terms are generally a factor of 6-10 times lower than the formation rates, however, the individual O3 destruction rates comprising the total destruction term varies in importance throughout the day, with losses due to NO2+OH dominating the mornings on both high and low O3 days. This would tend to indicate that there was an excess of NOx which coincides with the morning rush hour observed at the Moody Tower. The peak median O3 production rates during SHARP occurred during the middle of the day following the diurnal profile of j(NO2) and does not show the strong morning production rates that were found during TRAMP. During SHARP, the peak in the median diurnal net O3 production profile was ~16 ppbv/hr which occurred around solar noon, in contrast the same analysis for the Fall 2006 TRAMP campaign found a peak net O3 production of ~30 ppbv/hr around 11:00 AM. The overall reductions in O3 production due to clouds and aerosols during SHARP was ~2.9 ppbv/hr, compared to ~8 ppbv/hr during TRAMP.

Ambient ozone is the result of local photochemical production, surface deposition, and transport processes. Ground based ozone measurements, however, do not indicate whether ozone is locally produced or transported from other areas. The Measurement of Ozone Production Sensor, MOPS, deployed during SHARP monitored in real time the rate of photochemical production of ozone, P(O3), in ambient air. In addition, sensitivity of P(O3) to precursors was investigated under real conditions. MOPS measured P(O3) peaked in the late morning, with values between 15 ppbv h⁻¹ and 100 ppbv h⁻¹, although values of 40–80 ppbv h⁻¹ were typical for higher ozone days. Measured and calculated P(O3) had similar peak values but the calculated P(O3) tended to peak earlier in the morning when NO values were higher. Measured and modeled P(O3) had a similar dependence on NO, but the modeled P(O3) was only half the measured P(O3). This difference indicates possible missing radical sources in the box model with the RACM2 mechanism and thus has implications for the ability of air quality models to accurately predict ozone production rates.

The ozone production sensitivity to NOx or VOCs in Houston had a similar behavior for the following three campaigns: TexAQS 2000 (late summer), TRAMP 2006 (fall) and SHARP 2009 (spring); where it was VOC sensitive in the early morning and late afternoon but NOx sensitive throughout the afternoon. This behavior is typical of US urban areas. These results are independent of the differences between the measured and modeled OH and HO2. Note that in the afternoon the ozone sensitivity in SHARP 2009 has a longer NOx-sensitive period than TexAQS 2000 and TRAMP 2006, indicating that NOx control is an efficient approach for the O3 control in spring time.
Previous studies have found that there are significant daytime HONO levels existing in urban environments which can be photolyzed to produce OH radicals. During SHARP, the calculated HO\(_x\) production was dominated by photolysis of HONO in the early morning and by O\(_3\) photolysis in the midday. At night OH production was mainly from O\(_3\) reactions with alkenes. On average, the daily HO\(_x\) production rate was 23.8 ppbv day\(^{-1}\), of which 31\% is from O\(_3\) photolysis, 23\% from HONO photolysis, 12\% from HCHO photolysis, and 14\% from O\(_3\) reactions with alkenes. For HO\(_x\) loss, the clearly dominant process was the OH reaction with NO\(_2\), while the self-reactions between OH, HO\(_2\), RO\(_2\) become important in the afternoon when their concentrations reach the highest.

To further understand daytime HONO formation in Houston during SHARP, UCLA’s long path-DOAS observations of vertical concentration profiles of HONO, NO\(_2\), and other species were analyzed. Steady-state HONO mixing ratios were about 0.02 ppb in the late morning and decreased to 0.01 ppb in the afternoon. The elevated daytime HONO concentrations indicated a strong unknown source of HONO during the day. HONO mixing ratios also showed statistically significant vertical gradients throughout the day, with smaller mixing ratios aloft. This analysis concluded that the most likely source of daytime HONO is a photocatalytic conversion of NO\(_2\) on the ground. This conversion is proportional to solar irradiance, where we cannot clearly distinguish whether UV or visible wavelength ranges are more important and the NO\(_2\) concentration. The slope between this HONO production source and solar irradiance are quite similar on all days, allowing for the calculation of the following general parameterization of HONO formation in the lower 300m of the Houston atmosphere: 

\[
P_{\text{HONO}} = 3.3 \times 10^{-8} \text{m}^2\text{W}^{-1}\text{s}^{-1} \times (\text{visible solar irradiance}) \times [\text{NO}_2].
\]

The evaluation of role of ClNO\(_2\) as an early morning source of radicals and its contribution to O\(_3\) production found that without additional chlorine sources in the model, the modeled organic peroxy radicals initiated by Cl is less than 1\% of those initiated by OH and O\(_3\). The modeled concentrations of Cl and Cl\(_2\) are too low compared to previous observations, indicating that additional chlorine sources are needed in the model in order for the Cl chemistry to be important in photochemistry and ozone production. Modeled Cl concentrations in two sensitivity runs are comparable to the derived Cl concentrations from isoprene+Cl oxidation products during TexAQS2000, suggesting that Cl chemistry may be important in oxidation chemistry and ozone production if there is sufficient chlorine sources. This analysis indicates additional measurements of chlorine species are needed to assess the potential role of halogen chemistry in the Houston atmosphere.

Correlations between gaseous HNO\(_3\) and gas phase chloride were highly correlated on short (minutes to hours) time scales throughout the SHARP campaign. This correlation was discovered during the early days of SHARP campaign and re-analysis of the 2006 TRAMP data revealed that this phenomenon also occurred during that project. Peak mixing ratios of soluble gaseous Cl occurred during transport from south (i.e., clean conditions) with lower mixing ratios occurring in polluted air from the north and east. The opposite conditions (northerly winds/polluted conditions) resulted in peak HNO\(_3\) mixing ratios with a remarkably strong correlation with soluble Cl. Even during intervals with sustained northerly flow (relatively low Cl) daytime soluble Cl routinely exceeded 1 ppbv. Similar observations made during TexAQS 2006 on the Moody Tower and the NOAA vessel Ronald H. Brown indicate that abundant soluble Cl, linked with HNO\(_3\) by processes not yet understood, is characteristic of the Houston-Galveston Bay region during both spring and summer.
4. RECOMMENDATIONS FOR FUTURE STUDY
5. REFERENCES


6. APPENDIX A - MEASUREMENT PROCEDURES FROM QAPP (SHARP DATA COLLECTION)

Measurements were made from a height of 60 m a.g.l. on the roof balcony of the north Moody Tower, an 18-story dormitory on the campus of the University of Houston for more than 6 weeks. This is unique because all other surface sampling sites are much more sensitive to the nearby (i.e., within 100 m) local activities such as: traffic, parking lots, delivery trucks, railways, nocturnal surface drainage, etc. Prior to the 2006 TRAMP campaign conducted at this site, several small laboratories were constructed on the roof balcony of the north Moody Tower and significant power was added to support research instrumentation. A permanent 10-meter mast tower was erected on the site for measurement equipment and inlets. For the SHARP campaign in 2009, a temporary 6-meter walk-up scaffold tower was erected on the balcony to accommodate the needs of the visiting scientists.

6.1 ANALYTICAL METHODS

This section describes or references each process measurement or analytical method used. If applicable, modifications to EPA-approved or similarly validated methods are identified.

6.1.1 Meteorology

Meteorological parameters were measured continuously with sensors from RM Young, Vaisala, Setra, Texas Instruments, and Campbell Scientific. The meteorological sensors measure wind speed, wind direction, temperature, pressure, relative humidity, and precipitation. These measurements were collected in a data logger system via analog output voltages. This data was then recorded to the data acquisition PC for transmission and storage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind Speed</td>
<td>0 to 112 miles per hour</td>
</tr>
<tr>
<td>Wind Direction</td>
<td>0 to 360 degrees (°)</td>
</tr>
<tr>
<td>Temperature</td>
<td>-40 to +140° Fahrenheit</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>0 - 100%</td>
</tr>
<tr>
<td>Pressure</td>
<td>500 - 1100 mb or 600 - 1100 mb</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Infinite (0.01” per tip)</td>
</tr>
</tbody>
</table>

Specific performance requirements for the meteorological systems include:

- The RM Young anemometer was oriented to true north with a compass and/or GPS correction for magnetic variation.

Meteorological measurement methods are in accordance with U.S. Environmental Protection Agency *Quality Assurance Handbook Volume IV*, March 1995, methodology. Exceptions to the quality assurance requirements are noted below.
Wind Direction

Accuracy (absolute difference): ±3 degrees alignment, ±5 degrees overall.

Wind Speed

Accuracy (absolute difference): ±0.9 miles per hour (mph) or 1%, which ever is greater.

Temperature

Accuracy (absolute difference): 0.4-0.9 degrees Fahrenheit (°F).

Relative Humidity

Accuracy (absolute difference): ±2% 0-90% RH, ±3% 90-100% RH.

Pressure

Accuracy (absolute difference): ±0.6 mb.

Precipitation

Accuracy (absolute difference): ±1% rates up to 1”/hr, +0/-2.5% rates 1-2”/hr, +0/-3.5% rates 2-3”/hr.

6.1.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NO₃)

Measurement procedures used in this program were consistent with U.S. Environmental Protection Agency (EPA) 40 CFR Part 58, Appendices A through G, the Quality Assurance Handbooks for Air Pollution Measurement Systems, Volumes I and II, and the reference and equivalent methods designation criteria outlined in 40 CFR Part 53. The criteria pollutant sampling probes were sited in accordance with the EPA Quality Assurance Handbook, Volume II, Section 2.0.11 and EPA Ambient Monitoring Guidelines for the Prevention of Significant Deterioration. All materials were constructed of Teflon®.

Ambient air was supplied to the continuous analyzers through Teflon® tubing equipped with in-line particulate filters. The tubing was equipped with an in-line inverted funnel at the end to prevent large particles and water from entering the system.

The pollutant concentrations were automatically sampled and analyzed by the monitor. The output of the monitor was ASCII text via RS-232C serial connection. The serial outputs from the instruments were connected and sampled by data acquisition software on a PC every 10 seconds to form five-minute averages.

Ozone measurements were performed with a Thermo Environmental 49c UV photometer (EPA EQOA-0880-047). A Thermo Environmental 48c-TLE gas correlation wheel with internal zero and housing purge was used to measure carbon monoxide (EPA RFCA-0981-054).

Pulsed fluorescent technology was used to detect sulfur dioxide. SO₂ molecules are excited by an ultra violet (UV) light source and then decay to a lowered energy state producing a characteristic light that is measured by a photomultiplier tube. The pulsing of the UV source
lamp increases the optical intensity through which greater UV energy throughput and lower detectable SO₂ concentrations are realized.

NOₓ, NO₂, and NO₃ were measured with a 3-channel chemiluminescence detector. The NOₓ channel used a UV LED photolytic converter to photolyze NO₂ to NO for detection with chemiluminescence. NO₃ species were converted to NO at the sample inlet with a heated molybdenum cartridge at 320°C.

6.1.3 Photolysis Rates

Atmospheric photolysis frequencies (J values) can be calculated from the following equation:

\[ J(x) = \int S(\lambda, Z) \sigma(\lambda, T) \varphi(\lambda, T) \, d(\lambda) \]

where S is the zenith angle dependent solar actinic flux, \( \sigma \) is the absorption cross section as a function of wavelength and temperature, and \( \varphi \) is the photodissociation quantum yield as a function of wavelength and temperature. The UH Atmospheric Radiation Laboratory deployed the Scanning Actinic Flux Spectroradiometer (SAFS) to measure the solar actinic flux from 290-560 nm on the Moody Tower. The SAFS instrument is based on a \( 2\pi \) steradian light collector and a small, lightweight, computer controllable, double monochromator. The hemispherical light collectors consist of concentric hemispherical fused silica domes that are sandblasted and optimized to give nearly equivalent sensitivity for all zenith angles in a \( 2\pi \) steradian hemisphere. The normalized response is generally greater than 93% at zenith angles up to 85 degrees and has a negligible response above 95 degrees.

The monochromator (CVI Digikrom CM 112) has a focal length of 110 mm, wavelength precision of 0.1 nm, wavelength accuracy of +/-0.1 nm, stray light rejection of > 10^-9. The monochromator is coupled to a quartz hemispherical light collector with a custom UV fiber optic that tapers from a 1.6 mm diameter round form at the light collector end to a 0.6 mm X 4.2 mm rectangular shape matching the slit of the monochromator, for maximum light throughput. The photons exiting the monochromator are detected by a selected low dark current photomultiplier tube configured either in the current or photon counting mode. The monochromator is controlled via a serial port and the photomultiplier output as a function of wavelength is recorded on the data acquisition system through a 16 bit A/D converter or digitally. Actinic flux data from 290 to 460 nm was acquired in less than 30 seconds by stepping in 1 nm increments.

Photolysis frequencies of at least 20 important photolysis processes were calculated from the actinic flux spectra as a function of wavelength from the spectroradiometer including:

- \( O_3 + hv \rightarrow O(1D) + O_2 \)
- \( NO_2 + hv \rightarrow NO + O_3 \)
- \( HONO + hv \rightarrow OH + NO \)
- \( HO_2NO_2 + hv \rightarrow HO_2 + NO_2 \)
- \( HCHO + hv \rightarrow H + HCO \)
- \( HNO_3 + hv \rightarrow OH + NO_2 \)

The 2008 NASA JPL and IUPAC recommendations for the absorption cross section and quantum yield data with pressure and temperature dependences were used for the photolysis frequency calculations.
6.1.4 VOCs

VOC analysis sampling and measurement performed was based on developments by Veillerot et al. [1998]. The UH system has been described in Leuchner and Rappenglück [2010]. Briefly, a Perkin-Elmer VOC-system consisting of a Clarus 500 gas chromatograph with heart cut device and equipped with two flame ionization detectors and two columns (Alumina PLOT column and BP-1) for multi-dimensional gas chromatography is used. Every hour VOCs are sampled for 40 min and preconcentrated on a cold trap which contains carboneous sorbents and subsequently desorbed by a Turbomatrix 650 Automatic Thermal Desorber. Water was removed through a Nafion® dryer.

6.1.5 HNO₃, HONO, soluble Cl

The MC/IC measurement is based on concentrating soluble gases in ultrapure water with the mist chamber sampling device and using ion chromatography to quantify the concentration of ions in the solution. Standards were prepared from NIST traceable 1000 ppm solutions of the target ions. Determination of mixing ratios requires that the volume of aqueous solution and the volume of air sampled for each sample be known. Water volumes are determined with Kloehn syringe pumps, which are periodically calibrated gravimetrically, air volumes are measured with mass flow meters which are returned to vendor annually for certification.

Laboratory testing has shown that the mist chamber samplers quantitatively collect nitric and nitrous acids, when operated in field campaigns. However, these acids, especially nitric, are well known to be surface active, so passing efficiency of inlets are another concern. The research team has used this instrument to conduct numerous informal intercomparisons to assess the reliability of the technique to conduct numerous informal intercomparisons to assess the reliability of the technique for determination of nitric and nitrous acid (including the comparison of 7 techniques for HONO during the SHARP campaign). In addition, the nitric acid measurements have been formally assessed during three NASA airborne campaigns as part of the TabMEP program, and the team participated in the FIONA blind evaluation of 26 nitrous acid instruments conducted in the EUPHOR chamber in early 2010. These formal assessments have not found problems with this technique and system.

6.1.6 HONO

The UMiami HONO measurement is based on aqueous scrubbing followed by nitrite derivatization to a highly light-absorbing azo dye, which is then detected with liquid waveguide long path absorption photometry (LOPAP). The derivatization to the azo dye is completed through the following nitrite reactions with sulfanilamide (SA) and N-(1-naphthyl) ethylenediamine (NED):
A custom-built LOPAP instrument was deployed in this study. Ambient air was pulled through a light-shielded 10-turn glass coil sampler by a vacuum pump and the air flow rate was regulated at 1 L min\(^{-1}\) by a mass flow controller. A phosphate buffer with a concentration of 1.0 mmol L\(^{-1}\) was used as a scrubbing solution to collect HONO in the air sample. Due to its large effective Henry’s Law constant, HONO in the air was quantitatively collected in the samplers. After the separation from the gas phase, the scrubbing solution was mixed with SA/NED reagents. The mixture was then pumped through a Teflon derivatization tubing, where nitrite was converted to the azo dye via the above two reactions (R1 and R2). The aqueous sample finally flowed through a liquid waveguide capillary cell (LWCC, World Precision Instruments). The absorption of the light from a tungsten light source (FO-6000, World Precision Instruments) by azo dye in the sample was measured using a USB spectrometer (USB4000, Ocean Optics). The scrubbing solution and reagent solutions were delivered using a 16-channel peristaltic pump (Ismatec).

6.1.7 OH, HO\(_2\)

The inlet of the instrument was located at the top of a scaffolding or tower to minimize the impact from losses to the ground surfaces. The instrument operated continuously 24 h/day. The sampling frequency was 5 Hz while the instrument operated for 10 seconds in an on-line mode measuring OH and HO\(_2\) and 10 seconds in an off-line mode measuring the background signal.

The sampled air was pulled through a 1.5 mm diameter inlet, down a 20-cm long, 5-cm diameter tube, into a low-pressure (2-12 mBar) detection chambers by a vacuum pump (Eaton M45 Supercharger backed by a Leybold D25B vacuum pump) and was exhausted through a filter used to capture excess pump oil. A blower dilutes the exhaust further by mixing with 8000 L/min ambient air; therefore, the NO concentration at the exhaust is 0.8 ppm (as compared to 25 ppm OSHA/ACGIH/NIOSH TWA concentration, MSDS for Nitric Oxide, Matheson, Sep 19 2000).

Detection occurs in the detection chambers at the intersections of the airflow, the laser beams that are passed through multipass White cells, and the detector fields-of-view. The first detection cell encountered by the air stream is for OH. The second cell for HO\(_2\) is 10 cm downstream of the first. An injector loop positioned between the axes is used to add reagent NO for converting HO\(_2\) to OH. Because of the two-axis arrangement, the detection of OH and HO\(_2\) is simultaneous.

The laser is a combination of a Spectra-Physics T40-X30S-432Q diode-pumped frequency-doubled Nd:YAG laser (532 nm; 3 kHz repetition rate, 25 ns long pulses, 3 watts average power) which pumps a Harvard-modified Chromatix frequency-doubled dye laser.
[Wennberg et al., 1994]. This dye laser has an intracavity etalon that both narrows the laser line width to 3.5 GHz about the OH line width, and allows for tuning on and off the OH resonance. The laser is tuned on- and off- resonance with the OH transition (called on-line and off-line) every 10 seconds to determine OH fluorescence and background signals. The OH transition usually used is the Q1(2) near 308 nm. The UV laser power is typically 15-20 mW.

Collection optics gather about 8% of the fluorescence and send it to detectors behind narrow-band 308 nm interference filters. The detectors (Hamamatsu gated microchannel plate detectors) are gated on for approximately 300 ns to detect the OH fluorescence, approximately 60 ns after each laser pulse has cleared the detection cells. Two counter gates are used for each detector: one counts the OH fluorescence signal; a second counts the Rayleigh and chamber scattering for 50 ns during the laser pulse when the detector gate is off and the detector gain is more than 1000 times less.

A reference cell containing OH made on a hot filament indicates when the laser is on-line and off-line with the OH transition [Stevens et al., 1994]. The off-line position alternates between a longer and a shorter wavelength than the on-line position to test the flatness of the background signal. A spectral scan taken once every hour identifies the laser line and measures the background shape. An on-line dithering routine continually tests for the largest reference cell signal and adjusts the on-line position.

The GTHOS electronics resides in the rack inside the trailer. The PSMCU is the power supply and motor control unit; the DAU is the data acquisition unit. The computer uses real-time graphing and menu routines. Sampling occurs 5 times a second. The instrument operation uses an ASCII configuration file to initially set instrument operation. Many instrument functions are automated; a manual override allows for operator intervention. Both electronic text and strip charts are used to display data during the measurement.

The OH mixing ratio is found by the equation:

\[
\chi_{OH} = \frac{(\text{Signal}_{on-line} - \text{Signal}_{off-line})}{(C)},
\]

where \( C \) is the sensitivity, as is determined by laboratory and field calibrations. The continuous electronic observation of key parameters like laser power, cell pressure, temperature and Rayleigh scattering allows tracking of small variations in the performance of the instrument. The minimum detectable \([\text{OH}]\) is defined as the OH derived from twice the standard deviation of the background signal:

Peer reviewed papers covering the analytical methods used can be found in the following references:


6.1.8 O₃, NO₂, SO₂, HCHO, HONO, NO₃

The UCLA Long Path Differential Optical Absorption Spectrometer (LP-DOAS) instrument was deployed by UCLA atop the Moody Tower on UH campus during the SHARP measurements campaign in Houston, TX in spring 2009. Table 5-1 below provides a summary for the LP DOAS measurements during SHARP:

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Quantity Measured</th>
<th>Past Experience</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-Path Differential Optical Absorption Spectrometer (LP-DOAS)</td>
<td>In-situ, instantaneous, open air concentrations of: O₃, NO₂, HCHO, SO₂, HONO, and NO₃</td>
<td>Prior to SHARP, instrument has been deployed during many air quality field experiment, including TEXAQS-I at LaPorte in 2000 and during TRAMP on the Moody tower in 2006.</td>
<td>Instrument measures on three absorption lights path to retrieve vertical profiles</td>
</tr>
</tbody>
</table>

Table 5-1. Overview of the measurements within project H104C during the 2009 SHARP experiment.

Long Path Differential Optical Absorption Spectroscopy is a well-established method for detection and monitoring of atmospheric pollutants. It is an in-situ technique that measures the instantaneous, spectrally-resolved absorption features in a beam of white light traveling through the open atmosphere. The absorption path is folded once by one or more (in the case of vertical profiling) arrays of retroreflectors located at a distance of 2 to 5km from the instrument. DOAS method is widely used by government and private agencies to monitor ambient concentrations of pollutants such as NO₂, O₃ and SO₂. DOAS method is recognized by the United States Environmental Protection Agency as one of the automated reference methods [FR 65, 2000]: O₃ - EPA automatic reference method EQOA-0400-137; SO₂ - EPA automatic reference method EQSA-0400-138; NO₃ - EPA automatic reference method EQNA-0400-139.

The UCLA LP-DOAS instruments has been used in multiple field experiments including TEXAQS-I, at LaPorte in 2000 [Stutz et al., 2004 a,b] and during TRAMP on the UH campus in 2006. The instrument has been part of numerous intercomparison exercises [Dasgupta et al., 2005; McClenny et al, 2002; Geyer et al., 1999; Stutz, 2001].

The UCLA LP-DOAS instrument uses a double Newtonian telescope to send and receive a beam of white light from a Xe-arc lamp through the atmosphere. The receiving part of the telescope is coupled to a Czerny-Turner spectrograph with a focal length of 0.5 m (F = 6.9, 600 grooves/mm grating, temperature controlled at +30 ± 0.3 C) by a 200-um diameter quartz fiber. A photodiode array detector is used for the detection of the spectra from 300 nm to 380 nm (for O₃, NO₂, HONO, HCHO and SO₂) and 610 – 690nm (for NO₃) at a spectral resolution of ~0.5 nm. These spectra are stored in a PC for numerical analysis.

Sophisticated computer software extracts simultaneously from each measured spectrum the identity and concentration of all of the absorbing species present in the path of the beam,
solely based on well characterized published absorption cross-section data [Stutz and Platt, 1996; Platt and Stutz, 2008]. The LP-DOAS thus delivers in-situ and instantaneous “spectral images” of the current atmospheric composition along the absorption path.

6.2 CALIBRATION PROCEDURES

This section describes the calibration procedures for each of the methods described in this document.

6.2.1 Meteorology

A functional check of the equipment prior to the start of sampling and following any sensor or system change or adjustment was performed. Reference equipment used for the calibration and auditing of meteorological parameters is certified as accurate by the vendors. UH maintains the required equipment to calibrate the anemometers as needed.

6.2.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NO₃)

The University of Houston software performed automated QC checks (daily span/zero and periodic multipoint checks) on O₃, CO, SO₂, NO, NOₓ, and NO₃ monitors. QC procedures, control limits, and formulas to calculate QC statistics are given in standard operating procedures specific to the monitoring. The purpose of the span/zero and multipoint checks are to evaluate drift in the calibration curve of a monitor between calibrations, evaluate monitor performance, and assess measurement precision. Data validity decisions are based only on whether a QC test exceeds the failure limit. Quality Control tasks consisted of calibrations, maintenance, inspections, and record keeping.

The University of Houston maintains calibrated flow standards for calibrating instrument flowmeters. The University of Houston also operates TECO 49c-PS UV Photometric O₃ Primary Standard is compared, on a regular basis, with an EPA Region 6 Primary O₃ Photometer located in Houston. This primary standard was then used to check response of the O₃ monitor. A Thermo 146c & 146i multigas dilution systems were used in conjunction with NIST traceable CO, SO₂, NO, and NO₂ span gases certified by the vendor to generate test atmospheres to challenge the CO. The mass flow controllers in this calibrator were calibrated against NIST traceable BIOS DryCal flow standards.

Multipoint O₃ calibration checks were performed at the beginning of sampling and as needed because of instrument adjustment or repair. Several levels of O₃ calibration gas were introduced automatically at a programmed time into the inlet of the O₃ analyzer by a calibration system in the monitoring station. The levels nominally correspond to 160, 120, 75, 50, 25, and 0 ppbv. The O₃ calibration gas was derived from a primary standard.

The carbon monoxide (CO) calibration gas was derived from a NIST traceable span gas bottle that has been certified by the vendor. Multipoint point calibration checks were performed at the beginning of sampling and as needed. Multiple levels of calibration standard gases were introduced automatically at a programmed time into the inlet of the analyzers by a TECO 146i calibrator in the monitoring station. The levels nominally corresponded to 1000, 750, 500, 250, 100, and 0 ppbv.

NIST traceable span gas bottles that have been certified by the vendor containing 5 ppmv SO₂, 5 ppmv NO, 5 ppmv NO₂, and 10 ppmv CO in dry nitrogen, were used as gaseous
standards for the routine calibration of the CO, SO$_2$, and all NO instruments (i.e. O$_3$ via NO titration and chemiluminescence, NO, NO$_2$, NO$_y$).

A multipoint calibration of several calibration gas mixtures of SO$_2$, NO, and NO$_2$ were introduced automatically into the inlet of the analyzers by the calibrator. The levels correspond to approximately 100, 50, 25, 10, 5, and zero ppbv. Multipoint calibration checks were performed at the beginning of sampling and as needed because of instrument adjustments. The instrument responses along with reference values for all calibrations were recorded electronically.

Conversion efficiencies for the blue light converter (NO$_2$) and heated Mo (NO$_y$) were determined by multipoint challenges with NO$_2$, both from the cylinder and by gas phase titrations of O$_3$ + NO from the calibrator. Periodically, HNO$_3$ checks were also performed on the NO$_y$ system to check the conversion efficiency of the heated Mo converter.

The calibrator systems in the continuous monitoring for O$_3$, CO, Nitrogen Dioxide and Total Reactive Oxides of Nitrogen (NO/NO$_2$/NO$_y$) rely on the operation of flow controllers or flow restrictors to maintain a span gas flow and a dilution air flow at each of preset level. For each concentration level during a calibration or span check, the calibrator reports the mass flow rate from each controller to the data PC and were recorded with the measurement data. These flows, along with the cylinder concentrations, were then used to calculate the reference values for each level and gas.

6.2.3 Photolysis Rates

Wavelength accuracy was checked every 3 to 5 days by referencing to a low pressure mercury lamp line spectrum. Before and after the field deployment of the SAFS instrument, the absolute spectral sensitivity of the entire instrument was calibrated with three different FEL Quartz Tungsten Halogen (QTH) 1000 watt NIST traceable lamps with an uncertainty of 3-4% depending on the wavelength. Field spectral sensitivity calibrations were performed every 3 to 5 days at the same time as wavelength calibrations, using 300 W secondary QTH calibration lamps in a portable field calibration unit.

6.2.4 VOCs

The VOC GC system was calibrated using a 30 component EU Directive ozone precursor mixture provided by the UK National Physical Laboratory (NPL), Teddington/UK. This mixture contains VOCs in mixing ratios of about 4 ppbv (stated uncertainty below 2%).

The NPL standard is used to verify the stability of the linear carbon response of the GC. For identification purposes a 72 VOC standard in the range of 0.2-11.3 ppbv (stated uncertainty below 5%) provided by the National Center for Atmospheric Research (NCAR), Boulder/CO is used. This standard allows optimum identification and has been successfully used in recent intercomparisons by Rappenglück et al. [2006]. Both standards do not need any dilution and thus minimize errors and uncertainties arising from dilution methods. Instrument responses are correlated with concentration for each hydrocarbon species in the standard based on peak areas. Samples for zero tests are generated using a “dry compressed air” gas cylinder provided by Matheson-Trigas equipped with a Supelco Supelcarb HC Hydrocarbon Trap (volume 120 cc).

6.2.5 HNO$_3$, HONO, soluble Cl

Standards are prepared from NIST traceable 1000 ppm solutions of the target ions. To determine mixing ratios requires that we know the volume of aqueous solution and the volume...
of air sampled for each sample. Water volumes are determined with Kloehn syringe pumps, which are periodically calibrated gravimetrically, air volumes are measured with mass flow meters which are returned to vendor annually for certification.

Starting a run of the MC/IC entails making 10 liters of eluent for each of the ICs, and filling the feed water containers for the MC with ultrapure water (Milli Q). A mixed secondary standard is prepared by diluting NIST traceable primary standards in volumetric flask (primary standards are transferred by autopipette, but amount is confirmed gravimetrically). The highest working standard is then prepared by dilution of the secondary solution (again using volumetric and pipette). Lower concentration working standards (8-10 working standards in general) are prepared by serial dilution of the highest standard. When ICs have stabilized on the new eluent the standards are run. After the last standard 4 aliquots of the new feed water are sequentially run on each IC to confirm that the blanks for nitrite and nitrate are not detectable. (It has been found that the MilliQ system will remove both of these ions completely if the resin cartridges are not expended. To extend cartridge life during field campaigns MilliQ water is made from RO feed water in the lab in NH and shipped an adequate supply to the field, then run this ultapure water through Milli Q again immediately prior to use.) If the blanks are not zero the feed water is run through the Milli Q system again, using new cartridges if necessary.

This procedure is repeated when either the eluent runs nearly out (generally in the 48-84 hour time frame) depending on MC sampling frequency and the flow rate of IC eluent (latter depends on column and analytes of interest for given campaign). During an extended campaign the aim is to make eluent the same for each new run, so ICs stabilize very quickly. Therefore, standards are prepared for a new run before stopping the previous one, allowing maintenance and recalibration to be completed in less than 2 hours. The measurement group strives to perform this entire procedure at different times of day to avoid always losing data during the same part of any diel patterns that may be of interest at the study site.

Peak quantitation relies on chromatography software from Dionex. Each trace is manually checked to ensure that the "method" is treating peaks consistently, and that small changes in retention time during a 2-3.5 day long run (primarily caused by temperature variations) do not cause misidentification of peaks.

6.2.6 HONO

The LOPAP HONO instrument was calibrated using sodium nitrite (NaNO₂) standard solutions. The HONO mixing ratios in air samples can be calculated using the following equation:

\[
[HONO]_{pptv} = \frac{C_i F_l RT}{F_s P} \times 10^{12}
\]

where, \(C_i\) is nitrite concentration (mol L\(^{-1}\)) in the scrubbing solution, \(F_l\) is the flow rate (cm\(^3\) min\(^{-1}\)) of the scrubbing solution, \(F_s\) is the sampling air flow rate (L min\(^{-1}\)), \(R\) is the gas constant (8.314 Pa m\(^3\) K\(^{-1}\) mol\(^{-1}\)), and \(T\) and \(P\) are the temperature (294 K) and atmospheric pressure (101325 Pa) under which the mass flow controllers were calibrated. The detection limit of the LOPAP HONO instrument was about 3 pptv with a 2-minute integration time and the measurement uncertainty was about \(\pm 15\%\) at a 2\(\sigma\) confidence level.
6.2.7 \textbf{OH, HO}_2

The GTHOS instrument is calibrated approximately every two weeks. To determine the sensitivity (C) of the instrument, known amounts of OH and HO\textsubscript{2} are generated through the photolysis of water vapor at 185 nm with the subsequent reaction with O\textsubscript{2}.

\[
\text{H}_2\text{O} + \text{hv (}\lambda=185\text{ nm)} \rightarrow \text{H} + \text{OH}
\]

\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2
\]

About 50 slpm of ultra-zero air is run from the base of the tower up to the calibration system and passed through a de-ionized water bubbler. A variable air bypass to the water bubbler allows generate a range of different water concentrations (0-2%). The water concentration in the resultant mixture is monitored by a Vaisala solid state humidity sensor.

A low-pressure Hg lamp generates the actinic flux in a 2.5 x 1.2 cm irradiation region at the outlet of the calibration system to photolyze the water. The specific flux field at 185 nm has been characterized in the lab as a function of position and lamp power supply current using a PMT tied to a NIST-calibrated photodiode at the University of Colorado.

The produced OH and HO\textsubscript{2} concentrations are then calculated out of the flow rate of the air, the mixing ratio of the water in the air, the integrated actinic flux field and absolute cross section of water [7.3x10\textsuperscript{-20} cm\textsuperscript{2} molecule\textsuperscript{-1}]. Currently the upper-limit of the absolute calibration uncertainty (2\sigma confidence) is estimated at ± 32%. Hourly diagnostic tests and real time monitoring of key parameters like laser power, temperature and pressure at various positions of the instrument ensure the stability of the calibration in between calibrations.

Such a conservative estimate of uncertainty is not representative of the overall instrument precision, which is primarily governed by system performance and sample integration time. The limit-of-detection is typically 1x10\textsuperscript{5} molecules cm\textsuperscript{-3} for OH and 0.02 pptv for HO\textsubscript{2}. The integration time required to reach these limits is highly dependent on laser performance and the physical configuration of GTHOS for a field study. However, for SHARP, it was approximately ten minutes for OH and 20 seconds for HO\textsubscript{2}.

6.2.8 \textbf{O}_3, \textbf{NO}_2, \textbf{SO}_2, \textbf{HCHO}, \textbf{HONO}, \textbf{NO}_3

A calibration of the instrument is not necessary. Sampling artifacts are absent since the light path is in the open atmosphere. The LP-DOAS is therefore often considered an absolute measurement method for atmospheric trace gases. The accuracy of the DOAS system for most trace gases is ~3 - 5%. The accuracy is predominately determined by the uncertainties of the absorption cross section of each gas. Errors and detection limits are determined based on the noise and unexplained spectral structures in each atmospheric absorption spectrum, as explained in [Stutz and Platt, 1996; Platt and Stutz, 2008]. Table 5-2 lists the detection limits of the instrument during the 2009 SHARP experiment in Houston.
Table 5-2. Detection limits for trace gases measured by UCLA’s LP-DOAS during SHARP in Houston, 2009. Please note that DOAS calculates an error and detection limit for every absorption spectrum / data point. Detection limits vary with visibility and instrument behavior. We thus report the campaign average as well as the best detection limit during the campaign.

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>Average detection limit</th>
<th>Best detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>O_3</td>
<td>2 ppb</td>
<td>0.6 ppb</td>
</tr>
<tr>
<td>NO_2</td>
<td>80 ppt</td>
<td>20 ppt</td>
</tr>
<tr>
<td>SO_2</td>
<td>80 ppt</td>
<td>24 ppt</td>
</tr>
<tr>
<td>HCHO</td>
<td>200 ppt</td>
<td>70 ppt</td>
</tr>
<tr>
<td>HONO</td>
<td>32 ppt</td>
<td>15 ppt</td>
</tr>
<tr>
<td>NO_3</td>
<td>4 ppt</td>
<td>0.8 ppt</td>
</tr>
</tbody>
</table>
7. APPENDIX B - QUALITY METRICS FROM QAPP (QA/QC CHECKS) (SHARP DATA COLLECTION)

7.1 QC CHECKS

This section identifies the QC checks (e.g., blanks, control samples, duplicates, matrix spikes, surrogates), the frequencies for performing these checks, associated acceptance criteria, and corrective actions to be performed if acceptance criteria were not met for each process measurement and analytical method.

7.1.1 Meteorology

The following checks of the meteorological measurement instrumentation for wind speed, wind direction, temperature, relative humidity, pressure, and precipitation are performed by the operator during each visit to the site:

- Visually examine the position of the meteorological sensors. If the sensors are not mounted in the correct position, then the condition is documented in the logbook and corrected as soon as possible.

- Visually inspect the spinning of the propeller on the anemometer and the condition of the cups (i.e., missing blades, damage to the blades, etc.). If the blades are damaged and/or the motion of the blades is not what would be expected given current wind conditions, then the sensor and electronic checks are performed.

- Inspect the screen on the precipitation gauge for debris and clean as needed.

- Review the most recent display of the meteorological data and verify that the values recorded correspond to current atmospheric conditions. Note any discrepancies in the station logbook. The site operator will report any discrepancies noted during the site visits to the field operations and data management staff.
7.1.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NO₃)

The QA/QC checks for the O₃, CO, SO₂, NO, NO₂, and NO₃ measurements are described in the table below, along with acceptance criteria.

<table>
<thead>
<tr>
<th>Assessment Parameter</th>
<th>Quality Procedure</th>
<th>Control Minimum Frequency</th>
<th>Acceptance Criteria</th>
<th>Corrective Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement system contribution - Calibration</td>
<td>Precision/Linearity test – Multipoint calibration (multipoint calibration is not applicable for H₂O₂)</td>
<td>Once per month</td>
<td>Linear fit of 0.995 or better</td>
<td>Check calibrator settings. Recalibrate or repair.</td>
</tr>
<tr>
<td>Measurement system contribution – Span Check</td>
<td>Linearity test-span checks</td>
<td>Prior to and following installation, repair, or adjustment of equipment</td>
<td>Correlation coefficient &gt; 0.995</td>
<td>Check calibrator settings. Recalibrate or repair.</td>
</tr>
<tr>
<td>Measurement system contribution – Zero Check</td>
<td>Zero offset check</td>
<td>Once every 2 days:</td>
<td>Response below detection limit</td>
<td>Check zero air supply. Check for leaks. Adjust zero offset.</td>
</tr>
</tbody>
</table>

Table 6-1. QA/QC checks for the O₃, CO, SO₂, NO, NO₂, and NO₃ measurements.

7.1.3 Photolysis Rates

QA/QC checks for the photolysis rate measurements include wavelength calibrations and zero offset checks. Wavelength accuracy is checked every 3 to 5 days by referencing to a low pressure mercury lamp line spectrum. Zero offset corrections are evaluated each morning and evening while the sun is sufficiently below the horizon. Additionally, every 3 to 5 days and as needed, the collection optic is cleaned to remove dirt and debris.
7.1.4 VOCs

The QA/QC checks for the VOC measurements are described in the table below, along with acceptance criteria.

<table>
<thead>
<tr>
<th>Assessment Parameter</th>
<th>Quality Control Procedure</th>
<th>Minimum Frequency</th>
<th>Acceptance Criteria</th>
<th>Corrective Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement system contribution - Calibration</td>
<td>Precision/Linearity test – Multipoint calibration (multipoint calibration is not applicable for H$_2$O$_2$)</td>
<td>Once per month</td>
<td>Linear fit of 0.995 or better</td>
<td>Check calibrator settings. Recalibrate or repair.</td>
</tr>
<tr>
<td>Measurement system contribution – Span Check</td>
<td>Linearity test-span checks</td>
<td>Prior to and following installation, repair, or adjustment of equipment</td>
<td>Correlation coefficient &gt; 0.995</td>
<td>Check calibrator settings. Recalibrate or repair.</td>
</tr>
<tr>
<td>Measurement system contribution – Zero Check</td>
<td>Zero offset check</td>
<td>Once per month: SO$_2$, NO, NO$_2$ Daily: HCHO and H$_2$O$_2$ Twice a day: HONO</td>
<td>Response within 1% of full scale</td>
<td>Check zero air supply. Check for leaks. Adjust zero offset.</td>
</tr>
</tbody>
</table>

Table 6-2. QA/QC checks for the VOC measurements.

7.1.5 HNO$_3$, HONO, soluble Cl

Calibration of the IC systems as described in 5.2.5 above is at the heart of the MC/IC measurement. Comparisons of the calibration curves for all analytes to those made at beginning of previous runs require that slopes agree to within 1%. If not, working standards were remade and new curves created. In general, when calibration curves do not meet this standard the disagreement is large, reflecting failure of components in the IC (e.g., preconcentrator columns). Corrective action entails determining faulty parts and replacing.

7.1.6 HONO

HONO measurements based on chemical methods can suffer from some potential interferences. Therefore HONO instruments based on wet chemistry need to be carefully designed and characterized. In the laboratory, several candidate chemicals were tested, including NO$_2$, HNO$_3$, nitrate, and SO$_2$ for possible interferences in this HONO instrument. All tests showed that there is very little interference from those candidate chemicals.

In the field, another interference test was conducted using a dry annular denuder coated with sodium carbonate by connecting the denuder to the sampling inlet. The test was designed to characterize interferences from aerosols and other nitrogen species (e.g., NO$_3$, PAN,
and other organic nitrates) in air samples by removing HONO but retaining most of particles, NO$_2$, PAN or other organic nitrates in the air flow. The signals obtained from the ambient air through the denuder were essentially the same as the signals from zero air, indicating that there were no significant HONO interferences from the possible interfering species such as NO$_2$, aerosols, and organic nitrates in this environment.

The following QA/QC checks were performed during the field deployment to ensure the good HONO measurements:

- calibration using NaNO$_2$ standard or a HONO source once every 2-3 days;
- zero check by adding zero air — once a week (zero air from Pure Air Zero Air generator);
- using a dry annular denuder coated with sodium carbonate by connecting the denuder to the sampling inlet to check the interference to HONO measurements;
- measurements of air sampling flow rate and liquid flow rates—once a week.

### 7.1.7 OH, HO$_2$

Every hour on the half-hour the control system typically initiates an automatic diagnostic sequence in which various facets of instrument performance are evaluated. During this eight minute interval the spectrum of the OH fluorescence is scanned in the reference cell and in ambient air, to ensure proper alignment of the laser system. The HO$_2$ to OH conversion via NO is tested by varying the NO concentration. Possible laser induced interferences are tested by changing the laser power and monitoring the analyzed data for laser-power dependent signals. In addition, the laser is momentarily shut off to keep track of the offsets on the photodiodes that monitor the laser power at various positions in the detection system.

To ensure the accurate and proper performance of the instrument regularly maintenance work is required (Table 6-3).
<table>
<thead>
<tr>
<th>Type of scheduled maintenance</th>
<th>Aprox. time required</th>
<th>Accumulated Time in 7 days, week</th>
<th>Detail description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hourly diagnostic</td>
<td>8 min / 1 h</td>
<td>1355 min / week</td>
<td>Spectrum scan, dark noise detection, NO titration, C₃F₆ interference test</td>
</tr>
<tr>
<td>Daily maintenance</td>
<td>20 min / 24 h</td>
<td>140 min / week</td>
<td>Data management, exchange gas cylinder</td>
</tr>
<tr>
<td>Optical alignment</td>
<td>6 h / 3 days</td>
<td>840 min / week</td>
<td>Alignment of laser, quartz fibers, white cells</td>
</tr>
<tr>
<td>Bi-weekly maintenance</td>
<td>8 h / week</td>
<td>480 min / week</td>
<td>Calibration, laser dye replacement, pump maintenance</td>
</tr>
</tbody>
</table>

| Total time required for maintenance | 47 h / week |

Table 6-3. Regular maintenance work.

Acceptance criteria are applied to the OH and HO₂ measurements during the preliminary data analysis, which occurs when the data are retrieved from GTHOS the next morning. The criteria include the following:

- GTHOS sampling pressure, laser power, temperatures, and other housekeeping measurements within the range of acceptable operation;
- laser wavelength stability better than 90%;
- all GTHOS gas flows (e.g., N₂ for purging White cells, zero air for providing an internal sheath flow, hexafluoropropene for external removal of OH) are as expected;
- no insects caught in the inlet.

The corrective actions for the acceptance criteria are the following:

- GTHOS sampling pressure (vacuum pumps are checked and refurbished), laser power (laser is realigned, dye or dye cell window in dye laser is replaced), temperatures (additional cooling is added), and other housekeeping measurements within the range of acceptable operation;
- laser wavelength stability better than 90% (dye laser is re-aligned);
- all GTHOS gas flows (e.g., N₂ for purging White cells, zero air for providing an internal sheath flow, hexafluoropropene for external removal of OH) are as expected (gas cylinders are replaced; lines are checked for leaks); no insects caught in the inlet (insect is removed; inlet is examined).
7.1.8 O₃, NO₂, SO₂, HCHO, HONO, NO₃

LP-DOAS absorption spectra for which the light intensity during the measurement changed by more than 50% were rejected from the spectral analysis as these measurements are considered incomplete. All other spectra were analyzed. UCLA has the complete data set of this analysis. However, we submitted a data set to UH and HARC where measurements with large statistical errors (as determined by the spectral retrieval algorithm [see Platt and Stutz, 2008]) were removed. This is not done because we reject this data, but rather to avoid misuse of the data. It has been found in the past that many users of this data do not accurately consider the fact that each of our measurements has its own uncertainty. Often data points with high uncertainties were thus incorrectly interpreted. For the data set submitted to UH for archiving filtered observations with error larger than: 10ppb for O₃, 0.2ppb for NO₂, 0.1ppb for HONO, 0.5 ppb for HCHO, and 0.5ppb for SO₂ was delivered. The unfiltered data is available upon request.

7.2 ACCEPTANCE CRITERIA

This section addresses any additional project-specific QA objectives (e.g., completeness, mass balance) shall be presented, including acceptance criteria.

7.2.1 Meteorology

Acceptance criteria for meteorological measurements are listed below.

- Correct installation of sensors.
- Anemometer vane and propeller functioning as appropriate for the wind conditions.
- Precipitation gauge screen clear of debris.
- Data compares within reasonable limits with local weather stations under conditions when conditions should be expected to be reasonably uniform.

7.2.2 Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NOₓ)

See Table 6-1 in Section 6.1.2 above.

7.2.3 Photolysis Rates

The acceptance criteria for the wavelength calibrations is that the reference line must be within 0.5 nm of the published wavelength. If the difference is greater than 0.5 nm, the monochrometer is adjusted until the agreement is within the acceptance criteria. The zero offset corrections have no acceptance criteria, however they are used in data processing to correct for the baseline. Acceptance criteria for the cleaning is that the optic should be clear and free of dirt and debris after cleaning.

7.2.4 VOCs

See Table 6-2 in Section 6.1.2 above.
7.2.5 HNO$_3$, HONO, soluble Cl

Primary QA involves comparing the measurements made during each sample interval to preceding and subsequent samples (recall that the system uses 2 channels with independent MC samplers and ICs). Persistent large (>10 %) differences between the two channels when apparent ambient mixing ratios are not changing quickly indicate degradation of components in one channel, problems are investigated and resolved. For MC samplers the most common failure is breakthrough of the Teflon filter used to reflux the sampling solution, this can be visually confirmed and resolved by replacing the filter. More often, divergence of the two channels indicates incipient failure of IC components. In these cases the run is stopped, problem traced and fixed.

7.2.6 HONO

Acceptance criteria:
- The variation of the calibrations is less than 10%;
- Zero air background level is comparable to the detection limit;
- Interferences due to other chemicals in the air are insignificant compared to ambient HONO levels;
- The variation of the air sample flow rate is less than 5%. The decrease of the liquid flow rates (due to the aging of the autoanalysis tubing) is less than 10% and the decrease was corrected in the final data.

7.2.7 OH, HO$_2$

No additional acceptance criteria beyond those described in Section 6.1.7.

7.2.8 O$_3$, NO$_3$, SO$_2$, HCHO, HONO, NO$_3$

No additional acceptance criteria beyond those described in Section 6.1.8.
### 8. APPENDIX C – INORGANIC AND ORGANIC SPECIES USED IN OH REACTIVITY CALCULATIONS (SECTION 2.2)

<table>
<thead>
<tr>
<th>Inorganic Species</th>
<th>Definition</th>
<th>Carbon #</th>
<th>MW</th>
<th>Organic Species</th>
<th>Definition</th>
<th>Carbon #</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
<td>1</td>
<td>28</td>
<td>ACD</td>
<td>Acetaldehyde</td>
<td>2</td>
<td>44</td>
</tr>
<tr>
<td>CO2</td>
<td>Carbon dioxide</td>
<td>1</td>
<td>44</td>
<td>ACE</td>
<td>Acetylene</td>
<td>2</td>
<td>26</td>
</tr>
<tr>
<td>H2</td>
<td>Hydrogen</td>
<td>2</td>
<td>18</td>
<td>ACT</td>
<td>Acetone</td>
<td>3</td>
<td>58</td>
</tr>
<tr>
<td>H2O</td>
<td>Water</td>
<td>34</td>
<td>4</td>
<td>ACTP</td>
<td>Peroxy radicals formed from ACT</td>
<td>3</td>
<td>89</td>
</tr>
<tr>
<td>HNO3</td>
<td>Nitric acid</td>
<td>63</td>
<td>28</td>
<td>ADCN</td>
<td>Aromatic-NO3 adduct from PHEN</td>
<td>6</td>
<td>156</td>
</tr>
<tr>
<td>HNO4</td>
<td>Pernitric acid</td>
<td>79</td>
<td>58</td>
<td>ACDN</td>
<td>Aromatic-HO adduct from CSL</td>
<td>7</td>
<td>125</td>
</tr>
<tr>
<td>HO</td>
<td>Hydroxy radical</td>
<td>17</td>
<td>17</td>
<td>ALD</td>
<td>C3 and higher aldehydes</td>
<td>3</td>
<td>58</td>
</tr>
<tr>
<td>HO2</td>
<td>Hydroperoxy radical</td>
<td>33</td>
<td>17</td>
<td>API</td>
<td>Alpha-pinenes and other cyclic terpenes with one double bond</td>
<td>10</td>
<td>136</td>
</tr>
<tr>
<td>HONO</td>
<td>Nitrous acid</td>
<td>47</td>
<td>17</td>
<td>APIP</td>
<td>Peroxy radicals formed from API</td>
<td>10</td>
<td>185</td>
</tr>
<tr>
<td>N2</td>
<td>Nitrogen</td>
<td>28</td>
<td>28</td>
<td>BALD</td>
<td>Benzaldehyde and other aromatic aldehydes</td>
<td>7</td>
<td>106</td>
</tr>
<tr>
<td>N2O5</td>
<td>Dinitrogen pentoxide</td>
<td>108</td>
<td>28</td>
<td>BALP</td>
<td>Peroxy radicals formed from BALD</td>
<td>7</td>
<td>137</td>
</tr>
<tr>
<td>NO</td>
<td>Nitric oxide</td>
<td>30</td>
<td>28</td>
<td>BAL1</td>
<td>Peroxy radicals formed from BALD</td>
<td>7</td>
<td>121</td>
</tr>
<tr>
<td>NO2</td>
<td>Nitrogen dioxide</td>
<td>46</td>
<td>28</td>
<td>BAL2</td>
<td>Peroxy radicals formed from BALD</td>
<td>7</td>
<td>105</td>
</tr>
<tr>
<td>NO3</td>
<td>Nitrogen trioxide</td>
<td>62</td>
<td>28</td>
<td>BEN</td>
<td>Benzene</td>
<td>6</td>
<td>78</td>
</tr>
<tr>
<td>O1D</td>
<td>Excited state oxygen atom, O(1D)</td>
<td>16</td>
<td>32</td>
<td>CH4</td>
<td>Methane</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>O2</td>
<td>Oxygen</td>
<td>32</td>
<td>48</td>
<td>CHO</td>
<td>Phenoxy radical formed from CSL</td>
<td>7</td>
<td>139</td>
</tr>
<tr>
<td>O3P</td>
<td>Ground state oxygen atom, O(3P)</td>
<td>16</td>
<td>48</td>
<td>CSL</td>
<td>Cresol and other hydroxy substituted aromatics</td>
<td>7</td>
<td>108</td>
</tr>
<tr>
<td>SO2</td>
<td>Sulfur dioxide</td>
<td>64</td>
<td>48</td>
<td>DCB1</td>
<td>Unsaturated dicarbonyls</td>
<td>4.5</td>
<td>91</td>
</tr>
<tr>
<td>SULF</td>
<td>Sulfuric acid</td>
<td>98</td>
<td>48</td>
<td>DCB2</td>
<td>Unsaturated dicarbonyls</td>
<td>7</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DCB3</td>
<td>Unsaturated dicarbonyls</td>
<td>4</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DIEN</td>
<td>Butadiene and other anthropogenic dienes</td>
<td>4</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EOH</td>
<td>Ethanol</td>
<td>2</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EPX</td>
<td>Epoxide formed in TOL, XYL and XYO reactions</td>
<td>7.75</td>
<td>122.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ETE</td>
<td>Ethene</td>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ETEG</td>
<td>Ethylene glycol</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ETEP</td>
<td>Peroxy radicals formed from ETE</td>
<td>2</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ETH</td>
<td>Ethane</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ETHP</td>
<td>Peroxy radicals formed from ETH</td>
<td>2</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GLY</td>
<td>Glyoxal</td>
<td>2</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HC3</td>
<td>Alkanes, alcohols, esters and alkynes with HO rate constant (298 K, 1 atm) less than 3.4x10-12 cm3 s-1</td>
<td>3.6</td>
<td>44</td>
</tr>
<tr>
<td>Inorganic Species</td>
<td>Definition</td>
<td>Carbon #</td>
<td>MW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>------------</td>
<td>---------</td>
<td>-----</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC3P</td>
<td>Peroxy radicals formed from HC3</td>
<td>3.6</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC5</td>
<td>Alkanes, alcohols, esters and alkenes with HO rate constant (298 K, 1 atm) between 3.4x10-12 and 6.8x10-12 cm3 s-1</td>
<td>5.6</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC5P</td>
<td>Peroxy radicals formed from HC5</td>
<td>5.6</td>
<td>103</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC8</td>
<td>Alkanes, alcohols, esters and alkenes with HO rate constant (298 K, 1 atm) greater than 6.8x10-12 cm3 s-1</td>
<td>7.9</td>
<td>114</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC8P</td>
<td>Peroxy radicals formed from HC8</td>
<td>7.9</td>
<td>145</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
<td>1</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKET</td>
<td>Hydroxy ketone</td>
<td>3</td>
<td>74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISHP</td>
<td>Beta-hydroxy hydroperoxides from ISOP+HO2</td>
<td>5</td>
<td>118</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO</td>
<td>Isoprene</td>
<td>5</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISON</td>
<td>Beta-hydroxyalkynitrates from ISOP+NO alkynitrates from ISO+NO3</td>
<td>5</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISOP</td>
<td>Peroxy radicals formed from ISO+HO</td>
<td>5</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KET</td>
<td>Ketones</td>
<td>5</td>
<td>86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KETP</td>
<td>Peroxy radicals formed from KET</td>
<td>5</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIM</td>
<td>d-limonene and other cyclic diene-terpenes</td>
<td>10</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIMP</td>
<td>Peroxy radicals formed from LIM</td>
<td>10</td>
<td>185</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MACP</td>
<td>Peroxy radicals formed from MACR+HO</td>
<td>4</td>
<td>101</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MACR</td>
<td>Methacrolein</td>
<td>4</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAHP</td>
<td>Hydroperoxides from MACP+HO2</td>
<td>4</td>
<td>102</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCT</td>
<td>Methyl catechol</td>
<td>7</td>
<td>124</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCTO</td>
<td>Alkoxy radical formed from MCT+HO and MCT+NO3</td>
<td>7</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCTP</td>
<td>Radical formed from MCT+O3 reaction</td>
<td>7</td>
<td>172</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEK</td>
<td>Methyl ethyl ketone</td>
<td>4</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEKP</td>
<td>Peroxy radicals formed from MEK</td>
<td>4</td>
<td>103</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MGLY</td>
<td>Methylglyoxal and other aldehydes</td>
<td>3</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MO2</td>
<td>Methyl peroxy radical</td>
<td>1</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOH</td>
<td>Methanol</td>
<td>1</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPAN</td>
<td>Peroxymethacryloylnitrate and other higher peroxyacetyl nitrates from isoprene oxidation</td>
<td>4</td>
<td>148</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MVK</td>
<td>Methyl vinyl ketone</td>
<td>4</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MVKP</td>
<td>Peroxy radicals formed from MVK</td>
<td>4</td>
<td>119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NALD</td>
<td>Nitrooxyacetaldehyde</td>
<td>2</td>
<td>105</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLI</td>
<td>Internal alkenes</td>
<td>5</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLIP</td>
<td>Peroxy radicals formed from OLI</td>
<td>5</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganic Species</td>
<td>Definition</td>
<td>Carbon #</td>
<td>MW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>----------</td>
<td>------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLND</td>
<td>NO$_3$-alkene adduct reacting via decomposition</td>
<td>3</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLNN</td>
<td>NO$_3$-alkene adduct reacting to form carbonitrates + HO$_2$</td>
<td>3</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLT</td>
<td>Terminal alkenes</td>
<td>3.8</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLTP</td>
<td>Peroxy radicals formed from OLT</td>
<td>3.8</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ONIT</td>
<td>Organic nitrate</td>
<td>3.5</td>
<td>119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP1</td>
<td>Methyl hydrogen peroxide</td>
<td>1</td>
<td>48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OP2</td>
<td>Higher organic peroxides</td>
<td>2</td>
<td>62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORA1</td>
<td>Formic acid</td>
<td>1</td>
<td>46</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORA2</td>
<td>Acetic acid and higher acids</td>
<td>2</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORAP</td>
<td>Peroxy radical formed from ORA2 + HO reaction</td>
<td>2</td>
<td>109</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAA</td>
<td>Peroxyacetic acids and higher analogs</td>
<td>2</td>
<td>76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl nitrate and higher saturated PANs</td>
<td>2</td>
<td>121</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PER1</td>
<td>Peroxy intermediate formed from TOL</td>
<td>7.1</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PER2</td>
<td>Peroxy intermediate formed from TOL</td>
<td>7.1</td>
<td>157</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHEN</td>
<td>Phenol</td>
<td>6</td>
<td>94</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHO</td>
<td>Phenoxy radical formed from phenol</td>
<td>6</td>
<td>93</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPN</td>
<td>Peroxypropionyl nitrate</td>
<td>3</td>
<td>135</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCO3</td>
<td>Higher saturated acyl peroxy radicals</td>
<td>3</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROH</td>
<td>C$_3$ and higher alcohols</td>
<td>3</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TLP1</td>
<td>Peroxy radicals formed from TOL</td>
<td>7.1</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOL</td>
<td>Toluene and less reactive aromatics</td>
<td>7.1</td>
<td>92</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOLP</td>
<td>Peroxy radicals formed from TOL</td>
<td>7.1</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TR2</td>
<td>Peroxy radicals formed from TOL</td>
<td>7.1</td>
<td>109</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UALD</td>
<td>Unsaturated aldehydes</td>
<td>5</td>
<td>84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UALP</td>
<td>Peroxy radicals formed from UALD</td>
<td>5</td>
<td>133</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XO2</td>
<td>Accounts for addition NO to NO$_2$ conversions</td>
<td>N/a</td>
<td>N/a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XY2</td>
<td>Peroxy radicals formed from XYL</td>
<td>8.9</td>
<td>124</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XYL</td>
<td>M, p-xylene</td>
<td>8.9</td>
<td>106</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XYL1</td>
<td>Peroxy radicals formed from XYL</td>
<td>8.9</td>
<td>156</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XYL P</td>
<td>Peroxy radicals formed from XYL</td>
<td>8.9</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XYO</td>
<td>o-xylene</td>
<td>8.9</td>
<td>106</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XYO2</td>
<td>Peroxy radicals formed from XYO</td>
<td>8.9</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XYOP</td>
<td>Peroxy radicals formed from XYO</td>
<td>8.9</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>