EXECUTIVE SUMMARY

High ozone continues to be a major problem in many large U.S. cities, including Houston, Texas. Despite extensive efforts to address this problem, our understanding of the major precursors that control ozone formation is still highly uncertain and incomplete. One such major precursor is the toxic trace gas formaldehyde (CH_2O). This gas is produced in the atmosphere as an intermediate when virtually any volatile organic compound that is emitted into the atmosphere is oxidized, primarily by OH radicals. Formaldehyde subsequently rapidly decays in a matter of hours by reactions of these radicals and sunlight to produce ozone and additional radicals. These additional radicals then produce additional ozone. In Houston Texas the problem of ozone formation is particularly acute since the greater Houston-Galveston-Brazoria Metropolitan Area (HGBMA) is home to some of the largest petrochemical facilities in the United States. Highly reactive volatile organic compounds (HRVOC's) like propene and ethene, which are known to leak into the atmosphere from both normal and upset operations from these facilities, rapidly produce CH_2O and ultimately ozone.

Continued development of effective ozone control strategies requires a comprehensive understanding of the magnitude of various CH_2O sources, its photochemical production rates and pathways, and transport processes. Over the HGBMA one particularly important issue in this regard is our understanding of the relative importance of primary CH_2O sources relative to CH_2O produced from secondary photochemistry. Potential primary sources of CH_2O include any combustion process such as burning, flaring, and automotive emissions, as well as direct leaks from fugitive emissions from petrochemical facilities, to name a few sources. Photochemically produced CH_2O, which is also called secondary CH_2O, arises from the oxidation of the volatile organic sources discussed above. This also includes the oxidation of isoprene, a gas that is both emitted from certain trees as well as from petrochemical operations. Unfortunately, despite extensive efforts and advances from past studies, two competing views regarding the relative importance of primary versus secondary CH_2O sources over the greater HGBMA, which have appeared in the recent literature, have still not been resolved.

To address this critical issue as well as additional questions, a collaborative team from the University of Colorado (CU), the University of Maryland (UMD), and the NASA Goddard Space Flight Center (NGSFC) has embarked on the present project. In this study, we analyze high quality and fast airborne measurements of CH_2O measurements over Houston Texas acquired during two recent NASA airborne campaigns in 2013: Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) study; and 2) Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC[4]RS). The primary objectives of this study are to: 1) address the issue of CH_2O source apportionment over the HGBMA study area discussed above; 2) assess the current 2012 TCEQ emission inventories for CH_2O and its precursors; 3) assess our knowledge of the chemical mechanisms employed; 4) where possible document emission upsets; 5) identify petrochemical flaring events; and 6) confirm, where possible, the TCEQ DNPH CH_2O sampling results. The following tasks were performed (highlighted in italics) to accomplish these objectives, and the results for each task are listed with each task in boldface. Since Tasks 2 & 3 are closely related, these tasks are listed together.

1. *Prepare WRF and CMAQ input files and run the models using nested domains down to a horizontal resolution of 1 km using the 2012 TCEQ emission inventory. Once accomplished, carry out extensive model-measurement comparisons of CH_2O and other species to test the model accuracy throughout the HGBMA during the DISCOVER-AQ field campaign and assess current emission inventories where possible.*

    Modeling analysis employing the Community Multiscale Air Quality (CMAQ) model with Process Analysis, in very high-resolution mode (1 km resolution), driven by the WRF (Weather Research and Forecasting) meteorological model has been successfully developed, improved upon, and evaluated. This evaluation involved comparisons of various measured meteorological and trace chemical species concentrations (CH_2O, isoprene, CO, NO, NO_2, and O_3) with those simulated from CMAQ. Extensive CMAQ-Measurement comparisons were carried out for CH_2O and CO. Comparisons in the planetary boundary layer (PBL) and free troposphere (FT) showed reasonable daily agreement. Not considering Sept. 25, the absolute PBL biases (CMAQ-Meas.) for CH_2O and CO for all the remaining days are all relatively small. In the case of CH_2O, the average of all the daily mean PBL biases is -439 ± 392 pptv, and the average of all daily median biases is -319 ± 397 pptv. The average daily median bias percentage is -11.8 ± 15.7%. For CO, the average of all the daily mean PBL biases is -6.0 ± 14.7 ppbv, and the average of all daily median biases is -6.7 ± 14.0 ppbv. The corresponding daily median bias percentage for CO is -4.5 ± 10.7%.

    These small but persistently negative biases potentially reflect small underestimates in the emission inventories used in the calculations. However, we cannot rule out the possible contribution that CMAQ transports too much boundary layer air into the free troposphere, as has been observed on other occasions. Therefore, based on the above results, we have no firm evidence that the 2012 TCEQ emission inventory under normal conditions needs to be revised.

2. *Develop methods to identify, and provide tabulations of, time periods when sampling clearly identifiable direct emission sources of CH_2O close to their source. In this process, tabulate especially large emission sources observed from WP-3 observations and from reported petrochemical facility upsets. Where possible, estimate the magnitude of such events and provide an emission update. The CMAQ model will be re-run based on such updated emissions estimates. CMAQ output will be analyzed along the path of back trajectories to assess upstream influence. Kinematic back trajectories will be calculated from WRF model output using the WRF post-processing tool RIP (Read/Interpolate/Plot).*

3. *WP-3 observations of very large CH_2O concentrations in the 20 – 35-ppbv-range from the Sept. 25, 2013 flight during the first two circuits have identified this day as one to examine first employing the high resolution WRF-CMAQ model with updated emissions. This model will be analyzed along a forward trajectory calculated from the WRF output south to Smith Point to help in assessing the model chemistry by comparing the model and observations near and downwind of the source. Other significantly elevated time periods will be identified.*

Analysis of airborne CH_2O measurements over the greater HGBMA study area during the 2013 DISCOVER-AQ (9 sampling days over Houston) and SEAC[4]RS (1 sampling day over Houston) campaigns over the month of September revealed that only the September 25 sampling day showed exceptional high PBL CH_2O levels in excess of 30 ppbv, levels characteristic of our past measurements over the greater HGBMA study area in 2006 and 2000. All other sampling days in 2013 showed significantly lower PBL CH_2O levels in the 2 – 10 ppbv range. We presented an observational approach based upon fast aircraft measurements of correlations between CH_2O, O_3, CO, NO_x/NO_y ratios, and propene as a means of identifying time periods revealing enhanced sources of CH_2O. In this process, we have identified a number of such plumes, which based upon strong anti-correlations of O_3 with CO and high NO_x/NO_y ratios, indicated very fresh plumes concurrent with combustion sources. Most of these plumes were found in the vicinity of petrochemical facilities. A spreadsheet with the major plumes thus identified has been supplied with this report. At present, we do not have enough information to discern if such enhanced CH_2O: 1) originates directly from the combustion sources; 2) is produced during combustion chemically from its two major precursors propene and ethene; 3) occurs simultaneously from fugitive emissions of CH_2O, propene, and ethene; or 4) some combination of the above. Likewise, we do not have enough information to even speculate on the types of petrochemical combustion sources (e.g., flaring, fluidized catalytic cracking combustion, or other potential petrochemical combustion sources) that might be responsible for our observations, and therefore efforts to correlate which petrochemical stack that might be responsible for our observations is beyond the scope of this effort.

In our plume tabulations, the largest source of enhanced CH_2O associated with petrochemical combustion occurred during the 1st circuit on 9/25/13 right over the Baytown ExxonMobil complex around 9:48 am local time. A regression analysis of fast CH_2O and CO measurements produced a CH_2O/CO slope of 82.4 ± 5.4 pptv/ppbv (r^2 = 0.83, N = 51) over this plume. Four other days were identified where we acquired CH_2O/CO slopes over this same petrochemical complex at around the same local time (9/6/13, 9/12/13, 9/13/13, and 9/24/13). The grand average for these 4-days yields a CH_2O/CO slope of 30.4 ± 12.9 pptv/ppbv and a grand median slope of 24.3 pptv/ppbv, which is a factor of 2.7 to 3.4 times lower than that on 9/25/13. Based upon the 2013 Speciated Release Inventory for CH_2O and CO under normal operating conditions (supplied as a separate spreadsheet to AQRP) one would expect a normal operating CH_2O/CO slope of ~ 12 for all three ExxonMobil facilities combined, which is a factor of ~ 2.0 to 2.5 times lower than our 4-day grand (average/median) values. However, when one considers that this 4-day grand (average/median) reflects the sum of CH_2O released as well as CH_2O produced from propene and ethene released from these same facilities under normal operating conditions, we view this factor of 2.0 to 2.5 difference as a reasonable range of values for normal operating conditions. However, the factor of ~ 7 times higher measured slope on 9/25/13 relative to the normal operating Speciated Release Inventory is considerably higher, and in our opinion, suggests enhanced emissions of CH_2O and potentially its precursors on Sept. 25 emanating from the ExxonMobil complex during the morning hours, perhaps by as much as a factor of ~ 3 relative to the other sampling days. We presented additional evidence to further support this hypothesis. We also presented counter-arguments suggesting that some or

all of these enhancements may be caused by unique meteorology on this day (strong early morning inversion with a tightly capped boundary layer ~ 0.3-km) coupled with significantly enhanced ethene and propene emissions measured on this day by TCEQ's auto-GCs during the 5 -10 am hours over the nearby Lynchburg Ferry sampling site (from unknown sources). A more definitive assessment must await additional studies based upon Lagrangian model runs employing back trajectories, and this has been identified as one of the subject areas for a future proposal.

Likewise, efforts in providing individual enhanced emission estimates for various species in moles/hour emanating from the ExxonMobil complex on Sept. 25 that could then used to compare calculated and measured CH_2O concentrations downwind at Smith Point (Task 3) turned out to be far more complicated than originally anticipated. Additional input will be required to carry this out more rigorously than our initial attempts.

Despite our partial success in arriving at firm conclusions regarding Tasks 2&3, we were successful in identifying and highlighting the uniqueness of Sept. 25 relative to other DISCOVER-AQ flight days by highlighting the extensive enhanced CH_2O levels observed throughout nearly the entire HGBM study area over most of the sampling day. Aside from the early morning measurements over the ExxonMobil complex, the majority of these enhancements were found to be coincident with elevated propene (> 5 ppbv) and arise from CH_2O that is photochemically generated from its precursors.

4. *Examine the CMAQ model output run with the Process Analysis Mode to quantify the relative importance of primary emissions and secondary photochemical production of CH_2O throughout the HGBMA study area throughout the DISCOVER-AQ field campaign.*

The CMAQ model was run in Process Analysis Mode to assess primary and secondary sources of CH_2O throughout the greater HGBMA study area throughout the month of September 2013. CH_2O from secondary production sources (Production – Destruction) is approximately a factor of 5 times higher than direct emission sources in the planetary boundary layer (PBL) over the entire month of September and approximately a factor of 7 to 8 times the direct emission source for the atmosphere over the Houston-Galveston-Brazoria Metropolitan Area up to 5-km altitude. These results were further broken down as a function of hour for the entire month of September 2013. Over the 7 am – 7 pm daylight hours, the average ratio yields a value of ~ 8/1 within the PBL. This yields a secondary CH_2O contribution of ~ 89% over the daylight hours and this agrees well with the determination from Parrish et al. [2012] of ~ 92% based upon OH reactions of ethene and propene to produce CH_2O during daylight hours. It is important to note that these results cover the entire HGBMA throughout the entire month of September in 2013 and are not restricted to times and spatial domains where measurements have been acquired. We believe these September results should reasonably represent the results for the full year. However, additional modeling studies need to be run in future studies to definitely confirm this.

5. *Tabulate optimal time periods for select comparisons of airborne CH₂O measurements with ground and mobile CH₂O measurements, focusing on overflights close to DNPH cartridge sampling sites at Clinton, Deer Park and Channelview when sampling at such sites were operative. Compare integrated DNPH measurements with 24-hour synthesized integrated airborne measurements based upon the temporal dependence calculated from the CMAQ model and the WP-3 aircraft measurements acquired at different times throughout the day. To accomplish this, the CH₂O CMAQ model output at the surface will be corrected using WP-3 CH₂O measurements for overflights close to DNPH cartridge sampling sites. The corrected CMAQ model output will then be integrated over the 24-hour DNPH sampling times and a comparison carried out.*

   We assessed the accuracy of 24-hour integrated DNPH cartridge sampling measurements for CH₂O on one occasion at the Deer Park site on Sept. 13. This was carried out by comparing *24-hour synthesized integrated airborne measurements of CH₂O*, based upon the temporal dependence calculated from the CMAQ model and the WP-3 aircraft, with the DNPH cartridge sampling measurements at Deer Park. After applying a small correction to the CMAQ results to match the observations, we determined a 24-hour integrated CH₂O value of 3.799 ± 1.9 ppb on Sept. 13 at the Deer Park sampling site, a value that is in agreement with the integrated DNPH determination of 2.673 ppbv within the precision of the CMAQ value. This 30% difference is in line with the comparison slopes reported by Gilpin et al. [1997] between diode laser measurements of CH₂O standards and those retrieved by DNPH cartridge sampling methods.

6. *As a follow-up to Task 5, employ the CMAQ model output at the surface to identify potential nighttime emissions of CH₂O and/or its precursors.*

   The CMAQ modeling results in conjunction with ground-based auto-GC measurements of propene at the Deer Park sampling site point to possible evidence of nighttime emissions of CH₂O and/or its precursors, as has been suggested by Olauger et al. [2009].