

Quality Assurance Project Plan

Project 14-002

Analysis of Airborne Formaldehyde Data Over Houston Texas Acquired During the 2013 DISCOVER-AQ and SEAC⁴RS Campaigns

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Summary of Project

QAPP Category Number: III

Type of Project: Data Evaluation; Research or Development (Modeling)

QAPP Requirements: This QAPP requires descriptions of project description and objectives; organization and responsibilities; scientific approach; quality metrics; data analysis, interpretation, and management; reporting; and references.

QAPP Requirements:

Audits of Data Quality: 10% Required

Report of QA Findings: Required in final report

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DISTRIBUTION LIST

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1. Project Description and Objectives

1.1 Process and Environmental System to be Evaluated

Houston, Texas is one of the largest cities in the United States and certainly the largest city in Texas. The Houston-Galveston-Brazoria Metropolitan Area (HGBMA), an area with over five million inhabitants, often exhibits high ozone concentrations during stagnant wind conditions. The 2000 Texas Air Quality Study (TexAQS I), which investigated such events, revealed that highly reactive volatile organic compounds (HRVOC's, ethene, propene, 1,3-butadiene, and butenes) from very large petrochemical industrial facilities, particularly in and around the Houston Ship Channel, react with elevated oxides of nitrogen compounds [nitric oxide + nitrogen dioxide; $\text{NO}_x=(\text{NO} + \text{NO}_2)$] co-emitted from these facilities resulting in ozone (O_3) levels exceeding federal standards. A major finding of this study was that industrial emissions of these HRVOC's were underreported by these facilities by over an order of magnitude [Daum et al., 2003; Ryerson et al., 2003; and Wert et al., 2003a]. This important finding led to numerous follow-up studies and analyses for the HGBMA, including: the 2nd Texas Air Quality Study (TexAQS II) in 2005 and 2006 [Parrish et al., 2009]; the TexAQS II Radical and Aerosol Measurement Project (TRAMP) [Lefer et al., 2010]; the 2009 Study of Houston Atmospheric Radical Precursors (SHARP) [Olague et al., 2009]; and measurements and modeling analysis by Rappenglück et al. [2010], Johansson et al. [2013], and Parrish et al. [2012], to name a few of the many studies.

In all cases, significantly elevated levels (>30 parts-per-billion, ppbv) of formaldehyde (CH_2O) have been measured downwind of these petrochemical facilities arising from very rapid oxidation of the two most abundant HRVOC's in the HGBMA, ethene and propene, with the hydroxyl radical (OH). The analysis of Parrish et al. [2012], which is based upon CH_2O measurements by the Principle Investigator's (PI's) (Fried) group acquired during the 2000 and 2006 TexAQS studies, provides very convincing evidence of this enhanced CH_2O photochemical production, and enhanced production of O_3 that subsequently results when CH_2O rapidly decomposes, downwind of these petrochemical facilities located along the Houston Ship Channel. In addition to such secondary CH_2O production, this gas is also produced directly from incomplete fossil fuel combustion (automotive sources and industrial flares, as examples), biomass burning, and oxidation of isoprene and various terpenes as well as slower oxidation of alkanes and aromatic compounds [Fried et al., 1997 and 2003a,b and references therein]. A comprehensive understanding of O_3 production in the HGBMA therefore requires a comprehensive understanding of CH_2O emissions, photochemical production rates, and transport processes. Despite the extensive efforts and advances from past studies, there are still major gaps in our understanding of CH_2O in the HGBMA. As discussed by Parrish et al. [2012], quantifying the relative contributions of primary versus secondary sources of CH_2O is crucial for developing effective ozone control strategies. Unfortunately, the various studies above arrive at different conclusions regarding the relative contributions of primary (P) versus secondary (S) sources of CH_2O over the entire Houston-Galveston-Brazoria Metropolitan Area. Despite such divergent conclusions, both sources of CH_2O may actually be important in different regimes. Close to large petrochemical complexes direct emissions of CH_2O from flaring and other operations can indeed dominate, while further downwind secondary sources can become more important, particularly during summer months where photochemical activity is high. Because of the importance of this issue, it is highly desirable to revisit the issue of CH_2O source apportionment employing new data acquired in 2013, the most up-to-date emission inventories, as well as new analysis approaches.

Updating the emission inventories and temporal trends for CH₂O and its HRVOC precursors is another area requiring attention. The study by Washenfelder et al. [2010] based upon airborne measurements of various constituents (including our CH₂O measurements) carried out during the TexAQS I and II campaigns examined temporal trends for the 2000 to 2006-time period. Based upon trends in the ratios of ethene to NO_x and propene to NO_x observed for isolated petrochemical sources (6 facilities: Sweeny, Freeport, Chocolate Bayou, Texas City, Mont Belvieu, and the Houston Ship Channel), this study reported a 30% ± 30% decrease in these ratios over this 6-year period with significant day-to-day and within plume variability (-50% to +100%). The median CH₂O concentration, based upon our measurements, decreased by ~ 40% for this same sampling region over this 6 year period. It is important to note that this 40% drop in CH₂O is consistent with a ~ 30 to 40% drop in CH₂O from 24-hour averaged DNPH (2,4-dinitrophenylhydrazine) cartridge measurements over this same 6 year period. The Texas Commission on Environmental Quality (TCEQ) acquired such measurements every 6th day at the Clinton, Deer Park and Channelview sites, which are very close to the Houston Ship Channel. Despite this consistency, Washenfelder et al. [2010] point out that measured ratios for ethene to NO_x and propene to NO_x exceed emission inventories for the above 6 facilities by factors of 1.4–20 and 1–24, respectively, using the updated 2006-point source emission inventories provided by TCEQ. De Gouw et al. [2009], furthermore, report ethene emissions a factor of 6 higher than the 2006 TCEQ point source emission inventory for the Mont Belvieu industrial complex. Accurate predictions of future O₃ levels in the greater Houston area employing chemical transport models require that the above emission inventory discrepancies get resolved.

In addition, although there is consistency between the ground-based DNPH CH₂O temporal trends and those inferred by aircraft measurements between the 2000 and 2006 TexAQS studies, it is highly desirable to further extend these temporal comparisons out to 2013. A major benefit of this process is that the highly accurate in situ CH₂O measurements acquired on the P3 aircraft during spirals and missed approaches close to the DNPH sampling sites can be used to further validate the cartridge results under a variety of conditions. This is important since past studies by Herrington and Hays [2012] and by Gilpin et al. [1997] have shown that DNPH cartridge determinations of CH₂O can contain systematic biases even when potassium iodide (KI) O₃ traps are employed.

1.2 Project Purpose and Objectives

The overall objective of the present study is to address the 3 major issues discussed above: 1) source apportionment of CH₂O throughout the HGBMA; 2) updating the present emission inventories; and 3) validate and further extend the ground-based DNPH determinations of CH₂O with time. To accomplish this, the proposing team will analyze ambient CH₂O data they acquired on the P3 and DC-8 aircraft over the greater Houston area in the summer of 2013 during the DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) and SEAC⁴RS (Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys) studies. The Fried group deployed two highly sensitive, selective, accurate, and fast airborne spectrometers for CH₂O on the National Aeronautics and Space Administration (NASA's) P3 and DC-8 aircraft platforms during these campaigns. The analysis will rely on 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.

2. Organization and Responsibilities

2.1 Project Organization

This analysis on this project will be carried out at two different locations: the University of Colorado (CU) in Boulder, Colorado and the University of Maryland (UMD) in College Park, Maryland. The Co-PI's, Drs. Alan Fried and Christopher Loughner will closely coordinate on all project phases and results. Dr. Fried will serve as the main point of contact and will have overall responsibility for the research and associated quality assurance. Christopher Loughner, in close collaboration with Dr. Kenneth Pickering (UMD/Goddard team) will prepare and run WRF and CMAQ models using nested domains down to a horizontal resolution of 1 km using 2012 TCEQ emission inventory. The models will be run in various modes to: assess and update emission inventories; validate model meteorology and chemistry; and to quantify the relative importance of the three major CH₂O sources (primary emissions, secondary photochemical production, and regional transport). Both of these scientists have extensive experience and expertise with these models. Alan Fried and his team (CU team) will identify time periods when their CH₂O measurements on the NASA P3 and DC-8 aircraft platforms over Houston, Texas in 2013 indicated sampling from large petrochemical refinery plumes as well as other clearly identifiable sources (e.g., ship plumes, etc.) close to their source and downwind. Such time periods will provide the focus for these studies. The CU team will also be responsible for the tabulation of 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. Both the CU and UMD/Goddard teams will be involved in the determination of *24-hour synthesized integrated airborne measurements* based upon the temporal dependence calculated from the CMAQ model and the P3 aircraft measurements acquired at different times throughout the day. Such *synthesized* data will then be compared to the 24-hour integrated DNPH cartridge results.

This project will be overseen by Air Quality Research Program (AQRP) Project Manager Gary McGaughey and TCEQ Project Liaison Jim Smith. The scientists working on this project and their specific responsibilities are listed in Table 1. The CU team is primarily responsible for overall project, including the reporting and presentations, and for parts of Tasks 3,4, 5 and 6. The UMD/Goddard team is primarily responsible for work done under Tasks 1,2 and parts of Tasks 3,4, 5, 6.

Table 1: A list of project participants and their responsibilities

Participant	Project Responsibility
Dr. Alan Fried (CU team)	Co-Principal Investigator (Co-PI) with overall project responsibility for: identifying unique sampling periods for further analysis; for reviewing overall results; quality assurance; and for all reporting.
Drs. Dirk Richter, Petter Weibring, and James Walega (CU team)	Will assist Dr. Fried in all aspects of identifying unique sampling periods from their 2013 SEAC ⁴ RS and DISCOVER-AQ data sets for further analysis

Drs. Christopher Loughner and Kenneth Pickering (UMD/Goddard team)	Will prepare and run WRF and CMAQ models using nested domains down to a horizontal resolution of 1 km using 2012 TCEQ emission inventory. The models will be run in various modes to address the various objectives of this study.
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2.2 Project Schedule and Key Milestones

Table 2: Timeline of project

Task	2014							2015					
	June	J	A	S	O	N	Dec	Jan	F	M	A	M	June
Contract, Work Plan, QPP													
Task 1 - Prepare WRF & CMAQ													
Task 2 - Run Models, Update Emissions													
Task 3 - Sept. 25 Analysis													
Task 4 - Source Apportionment													
Task 5 - Aircraft/DNPH Comparisons													
Task 6 - Assess Other CH2O Sources													
Task 7 - Monthly Technical and Financial Reports													
Draft Final Report, AQRP Review													
AQRP/TCEQ Presentation													
Final Report													

Specific Implementation Tasks of Table 2

1. Prepare WRF and CMAQ input files and run the models using nested domains down to a horizontal resolution of 1 km using 2012 TCEQ emission inventory. Drs. Loughner & Pickering will be responsible for this task.
2. Identify time periods when sampling large petrochemical refinery plumes as well as other clearly identifiable sources (for example, ship plumes, etc.) close to their source and downwind, and iteratively using the high resolution WRF-CMAQ model with measurements at these times to arrive at updated emission rates for CH₂O. CMAQ will be re-run with the updated emissions. 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). The whole team, which includes Dr. Fried's group at the University of Colorado (CU) and Drs. Loughner & Pickering, will be responsible for this task.
3. Working with Sept. 25, 2013 data, a day with very favorable meteorological conditions and large emissions from the Baytown Exxon/Mobil petrochemical facility, the high resolution WRF-CMAQ model with updated emissions from (2) will be analyzed along a forward trajectory calculated from the WRF output south to Smith Point to help in validating the model meteorology and the chemistry. During the 2nd DISCOVER-AQ circuit (around noon local time) on this day the wind direction and speed changed. During the 1st circuit, the winds were out of the southwest with a well-defined capped inversion layer, allowing the P3 to capture a significant portion of the Exxon-Mobil petrochemical plume. During the 2nd circuit the wind direction shifted to the southeast and the speed diminished by a factor of ~ 4 to around 1.6 m/s. As a result the boundary layer over the ship channel all the way down to Smith Point experienced the significant direct Exxon-Mobil emissions as well as the photochemically

produced products down at Smith Point. This situation will provide an excellent opportunity to compare modeled concentrations with ground-based and airborne observations at Smith Point. The entire team will be involved in this activity.

4. Examine the CMAQ model output run with the Process Analysis Mode to quantify the relative importance of the three major CH₂O sources (primary emissions, secondary photochemical production, and regional transport), first on the Sept 25 plume and then on the HGBMA. Drs. Loughner & Pickering will be responsible for this task.
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. Dr. Fried and his team will be responsible for this task. Compare integrated DNPH measurements with *24-hour synthesized integrated airborne measurements* based upon the temporal dependence calculated from the CMAQ model and the P3 aircraft measurements acquired at different times throughout the day. The entire team will be responsible for this task.
6. Investigate where appropriate airborne CH₂O measurements as well as other measurements from the P3 and DC-8 flights to assess production of CH₂O from flares and isoprene using isoprene, MACR, and MVK measurements and CMAQ model output to derive a biogenic contribution to CH₂O in the HGBMA. The entire team will be responsible for this task.
7. Submission of monthly technical reports by the 8th day of each month with an accompanying financial report submitted by the 12th day of each month throughout the project duration. A final technical report will be submitted by June 30, 2015, preceded by a draft final report on May 20, 2015. Other reports (e.g., Executive Summary, Quartiles) will be submitted as requested by AQRP.

3. Scientific Approach

3.1 Data Needed

The 3 major objectives of this proposal are: 1) carrying out source apportionment of CH₂O throughout the HGBMA; 2) updating the present emission inventories; and 3) validating and further extending the ground-based DNPH determinations of CH₂O with time. This analysis will rely on the Community Multiscale Air Quality (CMAQ) model with input from WRF as well as high quality airborne data acquired on the NASA P3 and DC-8 platforms during the 2013 DISCOVER-AQ and SEAC⁴RS campaigns. The PI and his group operated CH₂O instruments on both aircraft (DISCOVER-AQ P3 Aircraft - Difference Frequency Generation Absorption Spectrometer, DFGAS; SEAC⁴RS DC-8 Aircraft – Compact Atmospheric Multispecies Spectrometer, CAMS) during these campaigns. Both instruments operate on the same fundamental approach employing infrared absorption using a strong and relatively isolated and well characterized CH₂O absorption line at 3.53- μ m as well as the same methods for data acquisition, zeroing, calibrating, sampling, and spectral fitting. The 1-second 1- σ limits of detection (LOD) for these instruments are: 40- 100 parts-per-trillion (pptv) for DFGAS, and 15- 30 pptv for CAMS. Additional measurements acquired on both aircraft, such as measurements of CO, various volatile organic compounds (VOCs), as well as many other trace gases and flight parameters will be employed in this analysis as needed. However, this analysis will rely most heavily on the CH₂O measurements acquired from both aircraft.

4. Quality Metrics

4.1 Quality Requirements

The required quality for the various input data that will be used in the WRF-CMAQ simulations is important for this study. Although the precise required accuracy is not straightforward, the accuracy of the data in the NASA database that will be employed here is typically within 10-20%, a range that is acceptable to achieve the goals of this study. The accuracy for the CH₂O measurements from both aircraft is typically around 4% of the ambient mixing ratio plus the respective LOD.

4.2.1 Procedures Employed to Ensure High Accuracy in the CH₂O Measurements

The discussion below will illuminate the extensive procedures employed in both instruments to ensure high measurement accuracy. A comprehensive discussion of the measurement principle, calibration, zeroing, data fitting, and many other aspects can be found in Weibring et al. [2006, 2007 and references therein] for both instruments. In both instruments, ambient air was continuously drawn through heated inlets mounted perpendicular to the aircraft flight direction, through pressure controllers, and ultimately through multipass sampling cells maintained at constant temperature and pressure. The absorption of mid-infrared (IR) laser light at 3.53- μm was detected after traversing pathlengths ranging between 89.6 and 100-m in the various instrument designs and CH₂O mixing ratios were determined by fitting ambient spectra acquired in 1-second increments for acquisition periods of 1-2 minutes in length to reference spectra obtained by introducing CH₂O calibration standards (5-18 ppbv range using onboard permeation sources) close to the inlet entrance multiple times throughout each flight, including on zero air and ambient air matrices. Background spectra were acquired before and after each ambient and calibration period. Such spectra were obtained employing well characterized on-board catalytic conversion systems of various designs, which generated CH₂O-free (zero) air that was added close to the inlet entrances at flow rates ~ 2 to 3 standard liter per minute (slm, defined here as 273 K and 1 atmosphere pressure) higher than cell flow rates. This frequent zeroing procedure very effectively captures and removes optical noise as well as residual outgassing from inlet line and cell contaminants. This is accomplished by averaging the background spectra before and after each ambient sampling period, and the resultant spectrum is then subtracted point-by-point from each 1-second ambient spectrum. The absolute CH₂O mixing ratios of the airborne calibration standards have been determined over the years based upon a variety of techniques, including: gravimetric methods, comparisons with Henry's Law standards, cartridge absorption followed by derivitizing and high performance liquid chromatography (HPLC) measurements, direct absorption employing the Beers-Lambert relationship using known spectroscopic parameters, and oxidative conversion of CH₂O to carbon dioxide (CO₂) followed by high precision CO₂ measurements [Veres et al., 2010]. The Fried group in the Gilpin et al. [1997] study utilized the first four methods and obtained agreement to within $\pm 6\%$, and the latter approach produced further agreement to within 5% of direct absorption. Since each of the spectrometers inherently measures absorbance, direct absorption has been employed to calibrate each of the onboard CH₂O standards before and after each field mission for the studies discussed in this proposal. During the 2013 campaigns, the CAMS instrument was further configured to routinely measure the calibration outputs before each flight by direct absorption.

This fundamental calibration method, which is fairly unique among airborne CH₂O instruments, allows us to add known calibration standards to nearly the entire inlet (standard addition on both ambient and zero air matrices) to check for inlet and cell line losses in flight. This

procedure together with frequent background acquisitions, where again nearly the entire inlet/sampling system is chemically zeroed, is important for high accuracy. This is particularly true when sampling immediately following large plumes containing high levels of various pollutants and aerosols from fires and other sources. Wert et al. [2002] showed that inlet exposure to CH₂O levels of 23 ppb for only 15 minutes produced subsequent CH₂O sampling artifacts from surface desorption by as much as 500 pptv for time periods as long as 30 minutes following a drop in the sampled concentration to zero. Background subtraction eliminated this artifact; a procedure instituted in all our airborne CH₂O measurements since 1996. In-flight calibrations and inlet zeroing were particularly important for the 2013 campaigns since fire plumes were frequently sampled by the DC-8 when flying outside of the Houston metropolitan area. Here CH₂O levels attained values as high as 690 ppbv during one event and were often many tens to several hundred ppbv.

Airborne *wing-tip-to-wing-tip* comparisons between CH₂O measurements acquired by the CAMS and DFGAS instruments during the 2012 Deep Convective Clouds and Chemistry Study (DC3) revealed good agreement to within the combined ambient measurement precisions. At ambient CH₂O values between 200 and 550 pptv, the differences in the mean values retrieved by both instruments ranged between 2 and 45 pptv. At higher ambient mixing ratios of 1.5 to 2 ppbv, the differences were larger (up to 228 pptv), but still within the mutual combined precisions. In fact, it is our belief that the higher ambient variability coupled with small differences in the air masses sampled both airplanes caused these higher discrepancies. Further, if one considers the fact that ambient CH₂O mixing ratios of importance for the present study typically range between 5 and 35 ppbv, such small discrepancies are inconsequential for this study.

4.2.2 Procedures for CMAQ Modeling

This project will utilize base case WRF and CMAQ model output run down to a horizontal resolution of 4 km that will be performed under DISCOVER-AQ funding. WRF and CMAQ model descriptions can be found on their respective webpages: www.wrf-model.org and www.cmaq-model.org. The WRF model will be driven by the North American Regional Reanalysis (NARR; <http://rda.ucar.edu/datasets/ds608.0/>) and Multi-scale Ultra-high Resolution (MUR) sea surface temperature analysis (http://podaac.jpl.nasa.gov/Multi-scale_Ultra-high_Resolution_MUR-SST) and the CMAQ model will utilize chemical initial and boundary conditions from the Model for Ozone And Related Chemical Tracers (MOZART) CTM (<https://www2.acd.ucar.edu/gcm/mozart>) and the CB05 chemical mechanism.

For this project, the 4 km model output will be used as initial and boundary conditions to run WRF and CMAQ with process analysis for a high-resolution 1 km domain covering the HGBMA during the DISCOVER-AQ field campaign. The 36, 12, 4, and 1 km modeling domains utilized in this study are shown in Figure 1. The CMAQ modeling domains will be slightly smaller than the WRF modeling domains (grid cells close to the horizontal edge of the WRF domains will not be included in the CMAQ domains). WRF and CMAQ will be evaluated with National Weather Service observations (meteorology), EPA's Air Quality System (AQS) observations (O₃ and particulate matter with particle diameters less than 2.5 micrometers (PM_{2.5})), and final quality assured DISCOVER-AQ ground-, and aircraft-based observations of O₃, carbon monoxide (CO), oxides of nitrogen compounds (nitric oxide + nitrogen dioxide, NO_x) and NO_x plus all other higher oxides of nitrogen gases (NO_y), and ammonia (NH₃) as well as a suite of VOC species, and a suite of aerosols). DISCOVER-AQ data and descriptions of the data are available at <http://www->

air.larc.nasa.gov/missions/discover-aq/discover-aq.html. Current figures along the flight track of the P3 will be created to compare model with observations. The following statistics will be calculated between the model results and observations to evaluate the model and are shown in Table 3: mean bias, normalized mean bias, normalized mean error, and root mean square error. Model-observation comparisons with the figures and statistics will be analyzed to ascertain why model errors and uncertainties exist (i.e., errors in the emissions, chemistry, and/or transport processes).

Sensitivity CMAQ simulations will be performed using the same model inputs as the base case with the exception of emissions input files CH₂O emissions will be altered based on CMAQ comparisons with observations made onboard the P3. The CMAQ sensitivity simulation will be evaluated using the same observations and methods discussed above.

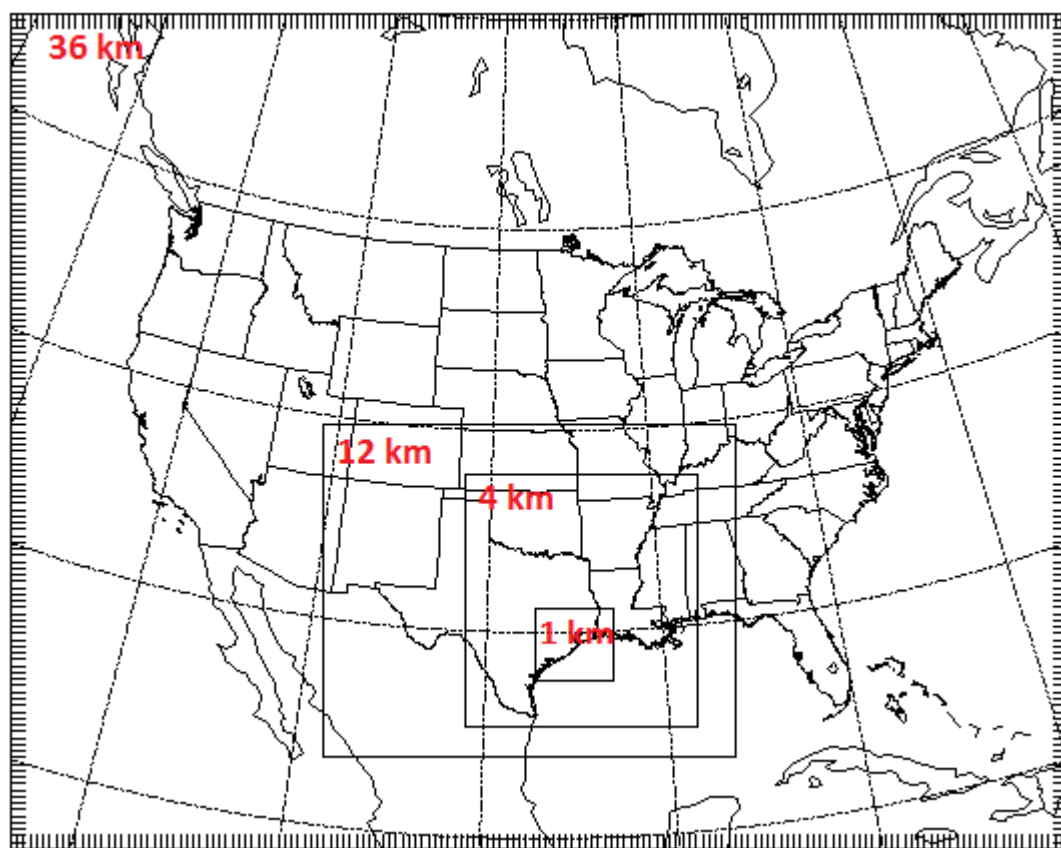


Figure 1: Location of the 36 km , 12 km, 4 km, and 1 km domains that will be used in the WRF and CMAQ modeling. Results from the 1 km domain will be utilized in this project.

Table 3: Statistics that will be calculated for performing the model evaluation.

Statistic	Equation
Mean Bias	$MB = \frac{1}{N} \sum_{i=1}^N (M_i - O_i)$
Normalized Mean Bias	$NMB = \frac{\sum_{i=1}^N (M_i - O_i)}{\sum_{i=1}^N O_i} \times 100\%$
Normalized Mean Error	$NME = \frac{\sum_{i=1}^N M_i - O_i }{\sum_{i=1}^N O_i} \times 100\%$
Root Mean-Square Error	$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (M_i - O_i)^2}$

4.3 Notes on Data Quality Requirements

We note that well-defined data quality requirements for the input data needed for this project do not exist. However, the accuracy of the airborne CH₂O measurements, one of the major inputs of this analysis, has been validated by extensive testing by the Fried group as well as from numerous ambient intercomparisons studies by Fried and his group [see for example, Wert et al., 2002, 2003, Gilpin 1997, and Fried et al. 2011].

5. Data Analysis, Interpretation, and Management

5.1 Data Reporting

The CU and UMD/Goddard teams will produce a series of technical memorandums to document each stage of this project and a draft final report and an approvable final report. Each technical memorandum documents the activities of each Task. The project team will issue monthly reports to the assigned AQRP project manager and a draft and fully revised final report at the end of the project. The reports will summarize steps that have been taken for quality assurance project data and results.

5.2 Data Validation

The entire team will be responsible for quality assurance (QA). Section 4.2.1 discusses at length the procedures that have been implemented in the validation of data acquired by measurements on the NASA P3 and DC-8 aircraft during the 2013 DISCOVER-AQ and SEAC⁴RS campaigns, respectively. Section 4.2.2 discusses how the high-resolution WRF and CMAQ model simulations will be evaluated. The primary measurements for this study, airborne CH₂O data, have estimated accuracies of around 4% + the LOD added in quadrature. The accuracy for the remainder of aircraft data required in the analysis have estimated accuracies in the 10-20%. The final DISCOVER-AQ CH₂O data has already been submitted to the final archive employing extensive quality control procedures. The SEAC⁴RS CH₂O data from the CAMS instrument operating on the NASA DC-8 will be submitted to the final archive over the next several months using the same data quality control procedures. The 10% data quality audit requirement will be satisfied by: (1)

carrying out rudimentary CH₂O comparisons when the two aircraft were either in close proximity or sampled the same boundary layer air mass over Houston close in time; (2) comparing aircraft CH₂O measurements with ground-based measurements of this gas by other study participants, when available, close in space and time; and (3) carrying out extensive cross checks by all the participants on the both the CMAQ input data and output results. At least 10% of CMAQ model output and inputs (i.e., emissions, initial and boundary conditions, modeling scripts, etc.) will be quality assured. Results from the QA will be included in the final report.

5.3 Data Summary for Reporting

The data sources that will be used as CMAQ input as well model set-up configurations will be summarized in a table. The updated emission inventories will be derived from this analysis will likewise be summarized in a table. As discussed in Task 3, favorable cases such as the Sept. 25 plume, high resolution WRF-CMAQ model results initialized with updated emissions from the Baytown Exxon/Mobil petrochemical facility will be tabulated at specific locations downwind at Smith Point and compared to both aircraft and ground-based observations at this location. This procedure will help in validating the model meteorology and the chemistry. Other similar favorable cases will be identified.

The high resolution WRF-CMAQ model with updated emissions will be run in the Process Analysis Mode (Task 4) to quantify the relative importance of the three major CH₂O sources (primary emissions, secondary photochemical production, and regional transport), first on the Sept 25 plume and then on other sources in the HGBMA. These results will be tabulated and compared to the results from other studies. As discussed in Task 5, 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, will be tabulated. Next, the 24-hour integrated DNPH measurements will be compared with *24-hour synthesized integrated airborne measurements* based upon the temporal dependence calculated from the CMAQ model and the P3 aircraft measurements acquired at different times throughout the day. These results will be tabulated and used as one means to validate the long-term CH₂O measurement trends provided by the DNPH measurements. An error analysis will be carried out on the *24-hour synthesized integrated airborne measurements* using the CMAQ model to provide error bounds on the DNPH measurements. Finally, other sources of CH₂O, from for example from flares and isoprene emissions, where appropriate will be quantified.

Comparisons between the model and aircraft observations will be presented as curtain figures following the path of the P3. Statistics between the model and observations will be presented in a table.

5.4 Data Storage

All primary input data employed in this project are, or will be, stored on the secure NASA data archive Web sites. These data along with model inputs and final outputs will be further securely archived during the project and transferred to the AQRP in electronic format following completion of this project. One means of doing this would be to transfer entire files onto an external hard drive that will be shipped to AQRP.

6. Reporting

6.1 Deliverables

1. Develop a project Work Plan, which includes a background introduction of this project, a statement of work (including goals, tasks, key personnel, deliverables, and schedule), and a budget with justification.
2. Develop a Quality Assurance Project Plan (QAPP).
3. Several reports will be submitted on a timely basis and at regular intervals. A description of the specific reports to be submitted and their due dates are outlined below. One report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). The lead PI will submit the reports, unless that responsibility is otherwise delegated with the approval of the Project Manager. All reports will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. Report templates and accessibility guidelines found on the AQRP website at <http://aqrp.ceer.utexas.edu/> will be followed.

Executive Summary

At the beginning of the project, an Executive Summary will be submitted to the Project Manager for use on the AQRP website. The Executive Summary will provide a brief description of the planned project activities, and will be written for a non-technical audience.

Due Date: Friday, May 30, 2014

Quarterly Reports

The Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Word doc file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

Due Dates:

Report	Period Covered	Due Date
Quarterly Report #1	June, July, August 2014	Friday, August 29, 2014
Quarterly Report #2	September, October, November 2014	Monday, December 1, 2014
Quarterly Report #3	December 2014, January & February 2015	Friday, February 27, 2015
Quarterly Report #4	March, April, May 2015	Friday, May 29, 2015
Quarterly Report #5	June, 2015	June 30, 2015

Technical Reports and Data Deliverables

Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison as a Word doc using the AQRP FY14-15 MTR Template found on the AQRP website.

Due Dates:

Report	Period Covered	Due Date
Technical Report #1	June 1 - 30, 2014	Tuesday, July 8, 2014
Technical Report #2	July 1 - 31, 2014	Friday, August 8, 2014
Technical Report #3	August 1 - 31, 2014	Monday, September 8, 2014
Technical Report #4	September 1 - 30, 2014	Wednesday, October 8, 2014
Technical Report #5	October 1 - 31, 2014	Monday, November 10, 2014
Technical Report #6	November 1 - 30 2014	Monday, December 8, 2014
Technical Report #7	December 1 - 31, 2014	Thursday, January 8, 2015
Technical Report #8	January 1 - 31, 2015	Monday, February 9, 2015
Technical Report #9	February 1 - 28, 2015	Monday, March 9, 2015
Technical Report #10	March 1 - 31, 2015	Wednesday, April 8, 2015
Technical Report #11	April 1 - 28, 2015	Friday, May 8, 2015
Technical Report #12	May 1 - 31, 2015	Monday, June 8, 2015
Project Data (observations, model inputs and outputs, and analysis products)	June 1, 2015 – June 30, 2015	July 30, 2015

Financial Status Reports

Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzone) by each institution on the project using the AQRP FY14-15 FSR Template found on the AQRP website.

Report	Period Covered	Due Date
FSR #1	June 1 - 30, 2014	Tuesday, July 15, 2014
FSR #2	July 1 - 31, 2014	Friday, August 15, 2014
FSR #3	August 1 - 31, 2014	Monday, September 15, 2014
FSR #4	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #5	October 1 - 31, 2014	Monday, November 17, 2014
FSR #6	November 1 - 30 2014	Monday, December 15, 2014
FSR #7	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #8	January 1 - 31, 2015	Monday, February 16, 2015
FSR #9	February 1 - 28, 2015	Monday, March 16, 2015
FSR #10	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #11	April 1 - 28, 2015	Friday, May 15, 2015
FSR #12	May 1 - 31, 2015	Monday, June 15, 2015
FSR #13	June 1 - 30, 2015, Final FSR	Wednesday, July 15, 2015

Draft Final Report

A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Due Date: Monday, May 18, 2015

Final Report

A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Due Date: Tuesday, June 30, 2015

Project Data

The final report and presentation will cover the results of tasks:

- a. 2.2.2 updated emission inventories for both CH₂O and its HRVOC precursors
- b. 2.2.3 employ opportunistic days like Sept. 25 and others to help in validating WRF-CMAQ model meteorology and the chemistry.
- c. 2.2.4 quantify the relative importance of the three-major CH₂O sources (primary emissions, secondary photochemical production, and regional transport) for select opportunistic days.
- d. 2.2.6 derive *24-hour synthesized integrated airborne measurements* and provide comparisons with integrated DNPB measurements. This will help to validate the DNPB temporal trends.
- e. 2.27 derive the biogenic contribution to CH₂O production over the HGBMA

All high-resolution WRF-CMAQ model runs, with updated emissions inventories and other inputs as well as outputs, will be submitted along with appropriate CH₂O measurement comparisons. In addition, all comparisons of the *24-hour synthesized integrated airborne measurements* with 24-hour integrated ground-based DNPB cartridge measurements will be submitted. These results will be submitted electronically, the exact format for which will be determined by AQRP.

6.2 Expected Final Products

An approved final report for this project will be prepared and submitted by end of this project. Multiple conference papers and/or peer-reviewed journal papers (e.g. papers in journal of Atmospheric Environment) on updated emission inventories, chemical mechanisms and/or CMAQ modeling are expected to be produced after completion of this project.

7.0 References

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