AQRP Monthly Technical Report

PROJECT TITLE	Analysis of Airborne Formaldehyde Data Over Houston Texas Acquired During the 2013 DISCOVER-AQ and SEAC^{4}RS Campaigns	PROJECT #	14-002
PROJECT PARTICIPANTS	Alan Fried, Christopher P. Loughner, and Ken Pickering	DATE SUBMITTED	6/8/2015
REPORTING PERIOD	**From:** May 1, 2015 **To:** May 31, 2015	REPORT #	8

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

Employing the completed 1 km CMAQ runs we: 1) carried out detailed comparisons with P3 formaldehyde (CH_2O) observations; 2) computed the 24-hour integrated CMAQ CH_2O concentration at the surface for September 13 over the Deer Park TCEQ sampling site and compared with the 24-hour integrated DNPH cartridge sampling method; 3) initiated efforts for establishing time periods when the P3 encountered fresh emissions of CH_2O from petrochemical facilities, most likely from flares, based upon fast correlations of CO-O_3-CH_2O and NO_x/NO_y ratios; and 4) initiated efforts in further analyzing isolated petrochemical plumes downwind of its primary source region.

Preliminary Analysis

Our March – May 2015 Quarterly Report presented more detailed temporal and spatial (CMAQ-Measurement) comparisons for CH_2O for two select days: September, 13, 2013 and September, 25, 2013. The former exemplifies typical results for many of the days studied, while the latter illustrates results from extreme petrochemical emission events from the Baytown Exxon/Mobil and Deer Park facilities later in the month. Since these activities were carried out in May, we repeat the results and discussion presented in the Quarterly Report here with some additional supporting evidence.

Figure 1 shows this comparison for the 2nd P3 circuit on September 13. It is important to note that in contrast to model results, which calculate relatively constant 5-minute average CH_2O concentrations in ± 1km grid boxes, the 1-second P3 CH_2O measurements often reflect large changes in airmasses as the P3 traverses ~ 0.1km each second. This results in large measurement variance compared to model results. To facilitate comparisons, the longer temporally and spatially-averaged model results are determined at each 1-second P3 sampling time. Although the true variance is smoothed out in the model, one can still compare results for select time periods for a given spatial region with common sources at relatively constant altitudes. In Figures 1& 2, these time periods are denoted by dark horizontal traces, where the blue and red lines respectively represent the average CH_2O measurement and CMAQ model results. These

traces are only meant to graphically show the overall biases for the select time periods. The actual (CMAQ-Measurement) biases are determined by point-to-point differences over the select time periods and these values along with their standard deviations are given in the plots. As can be seen, although there are differences, the measurements and model values follow the same overall trends. Fig. 1 shows 4 FT and 3 PBL time periods for comparison. Combining the 3 PBL legs yields an average overall (CMAQ-Measurement) difference of -705 ± 158 pptv (-17% ± 4%), which we attribute to low biases in CH_2O and its precursor emission sources employed as input in the CMAQ model. Our follow up studies will attempt to address this. Not surprising, the largest bias occurs during the PBL leg from Smith Point to Moody Tower over Galveston Bay and the Houston Ship channel, where many of the petrochemical facilities are located. The corresponding PBL comparisons for CO yield a much smaller (CMAQ-Measurement) bias of -2.8 ± 1.5 ppbv (-2.2% ± 1.2%), which supports the veracity of the CMAQ model results both in terms of CO emissions and transport. By contrast, three of the four FT comparisons for both CH_2O (CMAQ-Measurement = 660 ± 250 pptv) and CO (CMAQ-Measurement = 39.8 ± 2.0 ppbv, 50.5% ± 1.4%) suggest a problem in the FT CMAQ calculations, perhaps in the transport from the PBL to the FT during this day.
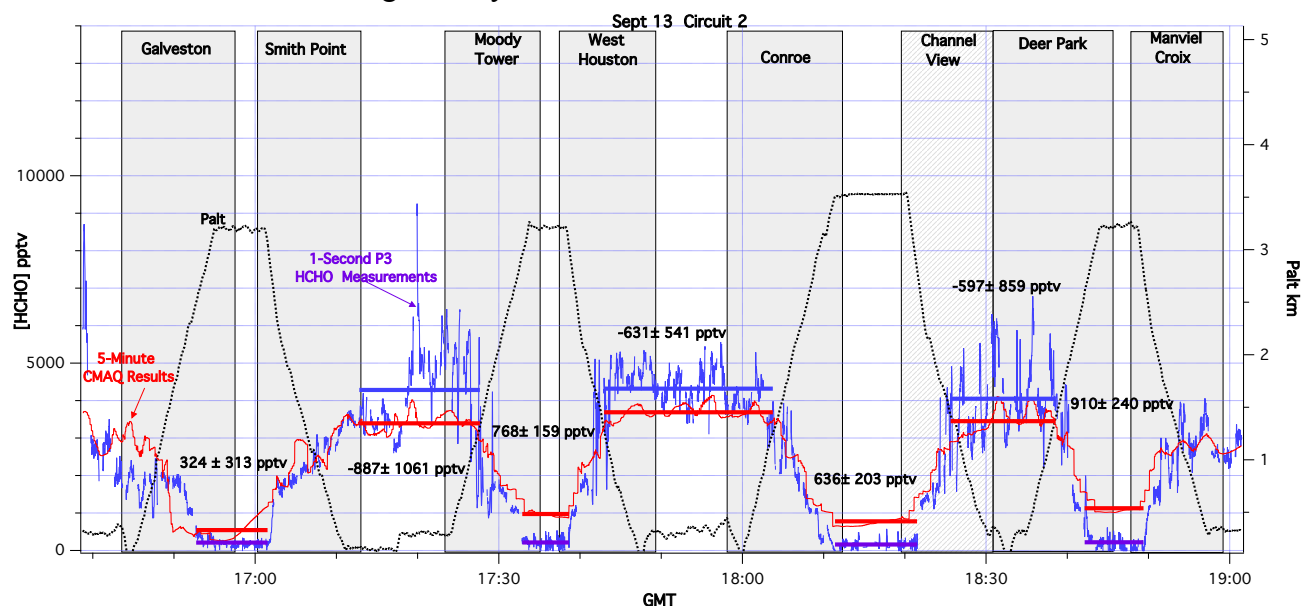

Figure 1: P3 CH_2O measurements (1second data, blue trace) and 5-minute CMAQ model results (red trace) for the 8 spiral sites during the 2nd circuit of the September 13, 2013 DISCOVER-AQ flight. The dark horizontal blue and red traces are averaged values over the select PBL and FT time periods, with the resultant point-by-point average (CMAQ-Measurement) differences and standard deviation given for each period.

Figure 2 shows the corresponding plot for the 1st circuit of Sept. 25, which is a day with significant petrochemical emissions of CH_2O (due to flaring) and its highly reactive precursors ethene and propene, as well as significant photochemical production of CH_2O downwind. The results for the select periods shown in Fig. 2 for this day (4 FT legs, and 4 PBL legs) are significantly different than Sept. 13. The composite PBL results yield an average point-by-point CH_2O (CMAQ-Measurement) difference of -5025 ± 4492 pptv (-45% ± 32%) and a corresponding CO difference of -124 ± 53 ppbv (-42% ± 9%), values that reflect significant petrochemical emissions that are not accounted for in the CMAQ emissions input for both CH_2O and CO. With the exception of the Smith Point PBL leg (during this 1st circuit), the remaining 3 PBL legs over the Baytown Exxon/Mobil complex, over central Houston, and over the Deer Park Shell facility, all show significant model negative biases, with the largest bias over the Exxon/Mobil facility, where we have evidence of a flaring event. The 4 FT legs of Fig. 2 also

show different behavior than Sept. 13. In contrast to the potential CMAQ transport issue discussed, the FT comparisons of Sept. 25 yield excellent agreement for both CH$_2$O (average (CMAQ-Measurement) = -14 ± 57 pptv, -2% ± 18%) and CO (average (CMAQ-Measurement) = 11 ± 2 ppb, 13% ±2%).
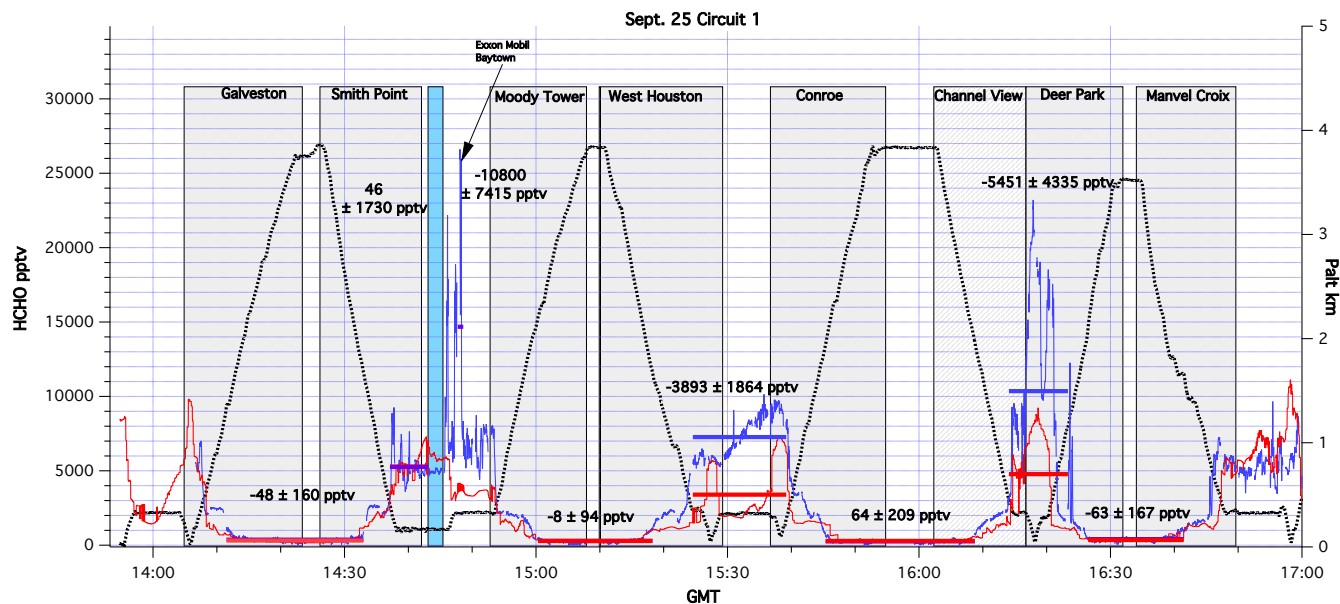

Figure 2: P3 measurements and CMAQ model results for Sept. 25, 2013 in the same format as Fig 2. This time period accentuates emission inventory biases.

Figure 3 below shows the time series plot around the ExxonMobil complex during the 1st Circuit in greater detail. Although this plot is quite busy, showing numerous fast tracers, it depicts the analysis methods we have initiated to identify the types of plumes encountered by the P3. As can be seen, fast measurements of CH$_2$O, CO, and propene from the P3 are highly correlated in many instances. In addition, O$_3$ in many instances is also correlated with these tracers, and this is indicative of air that has been oxidized. This plot also shows the NO$_x$/NO$_y$ ratios as an indicator of the air mass age being sampled. High ratios from ~ 0.9 to 1 generally indicates very fresh plumes, as most of the NO$_y$ species is comprised of NO and NO$_2$ from their emission sources. As the air mass ages, the NO$_x$ undergoes oxidation to form species such as HNO$_3$, PAN, alkyl nitrates and other species. The resulting NO$_x$/NO$_y$ ratios drop. Directly over the ExxonMobil facility around 14:48, the O$_3$ strongly anti-correlates with CH$_2$O, CO, and propene, as the O$_3$ is temporarily titrated out by fresh NO emissions. Likewise, the NO$_x$/NO$_y$ ratios here are near 1, and all these observations strongly indicate the influence of direct emission sources from the ExxonMobil complex, most likely from flaring. The P3 cameras also show the intercept of smoke plumes during this time period. We are currently analyzing all the P3 time periods to identify similar events as well as events indicating the presence of clear photochemical oxidation. In this analysis, the O$_3$-CO-CH$_2$O slopes and correlation coefficients are being tabulated, and in cases where interesting features are identified, we are following up with CMAQ back trajectories to pinpoint the source region. The results of this analysis will be presented in next month's report.
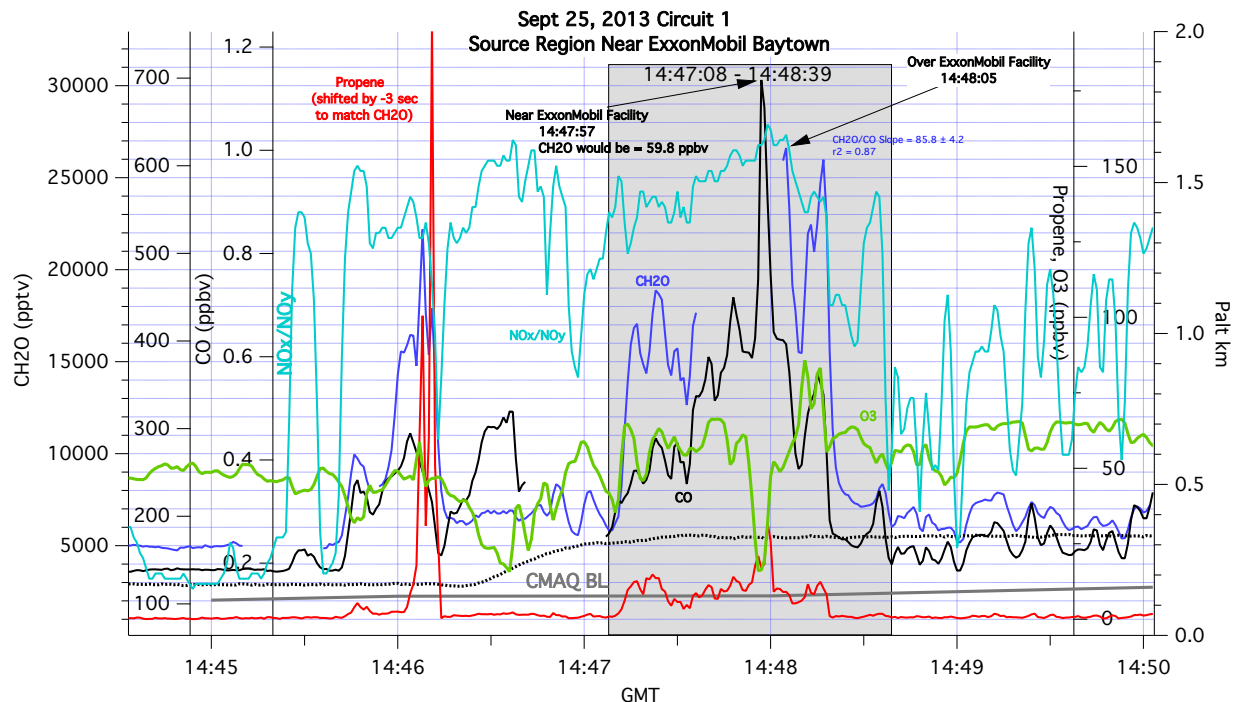
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Figure 3: Time series plot of CH_2O, CO, O_3, propene, and NO_x/NO_y ratios during the 1st Circuit of Sept. 25, 2013 near the ExxonMobil Baytown complex.

Figure 4 depicts the typical P3 flight profile employed, highlighting the sampling altitudes, spiral sites, and major facilities, sized by the estimated 2013 VOC emission rates in tons/day.
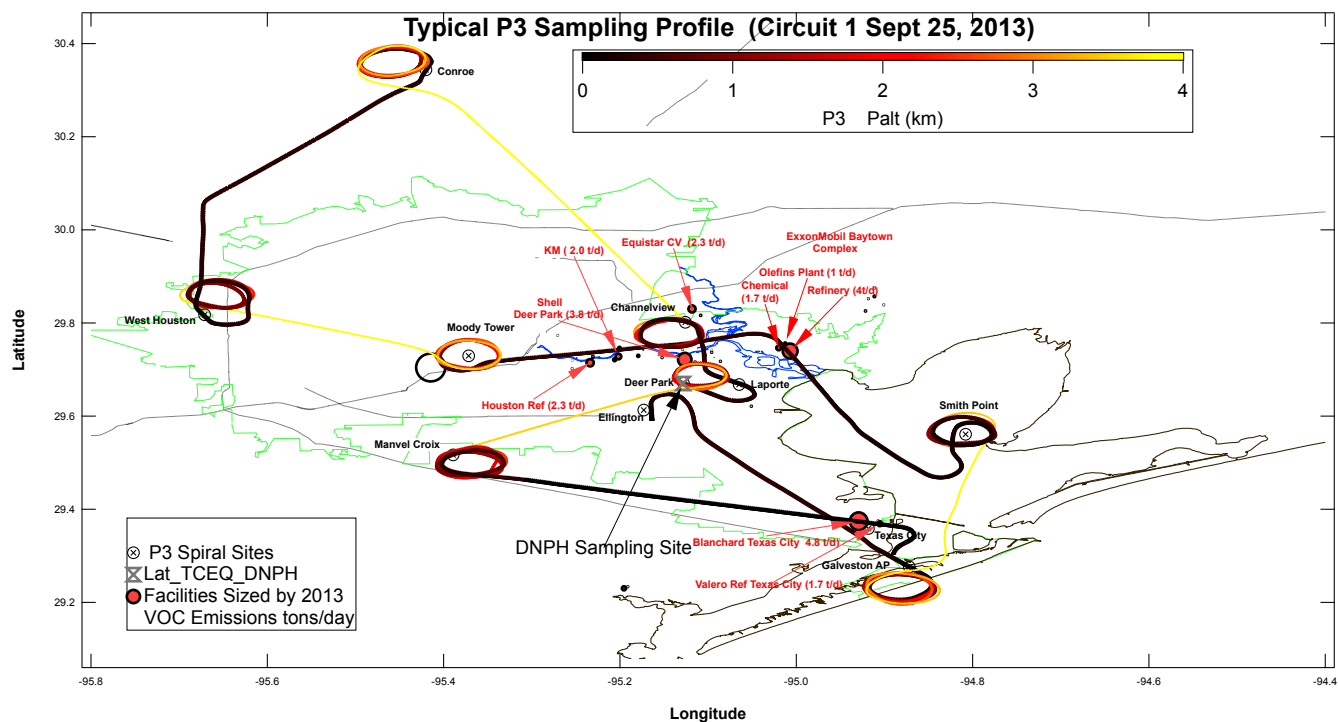

Figure 4: Typical P3 flight profiles during the 2013 DISCOVER-AQ Studies employed. We only show the top 8 VOC facility emission sites.

Figure 5 shows detailed daily comparisons between 1km CMAQ modeled CH_2O and the P3 observations in the PBL for the entire month of September in 2013. The PBL sampling legs are highlighted in Fig. 4 by darker flight legs between spiral locations. These plots, which are similar to those presented in last month's report and in Fig. 1&2 here, present the comparisons for the more complete dataset. Figure 5 also includes the mixing ratios (mean ± 1σ and median) for both the measurements and modeled values in addition to the daily mean and median biases (CMAQ-Measurement).
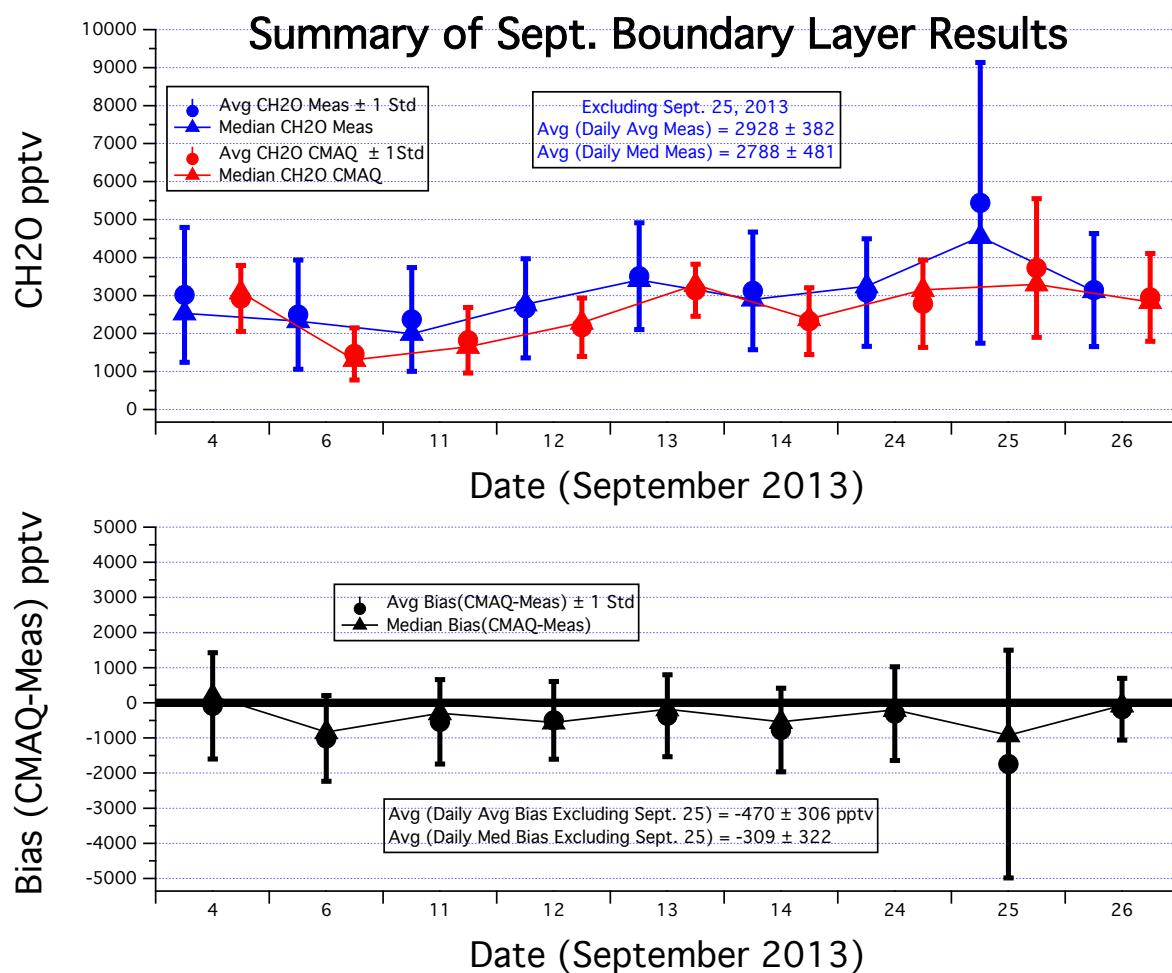

Figure 5: Comparison of daily CH_2O mixing ratios from the P3 observations and the 1km CMAQ model results.

As can be seen, the daily mean model and measurement averages overlap within the mutual imprecision limits in the upper plot. However, the bottom plot is the more meaningful plot. Here we display daily (CMAQ-Measurements) biases based upon point-by-point comparisons. As indicated previously, the model is biased low in many cases, most likely because the precursor emission sources in the model input are too low. These emissions sources are from the 2012 emission inventory. However, in 7 of the 9 daily comparisons, the median biases are all within 600 pptv, and in 5 of the 9 cases, median biases are all within 300 pptv. Excluding Sept. 25, which is a major outlier, the overall average of the daily median bias for the remaining 8 flights is -309 ± 322 pptv (11.7% ± 12.9%). We are presently assessing if we can further identify sampling conditions (sampling location, wind direction, wind speed, proximity to large emission sources, airmass age, etc.) that may give rise to smaller or larger biases, and these results will be

presented in subsequent reports. In this analysis we will also identify isolated plumes by which to further assess the present emission inventories.

In the final effort this month, we studied in greater detail the PBL measurements over the Deer Park TCEQ sampling site on September 13, 2013. As Fig. 4 shows, the P3 carried out measurements very close to this sampling site on each of 3 nominal sampling circuits every P3 flight day. On Sept. 13, 2013 the 24-hour DNPH sampling system for CH_2O was operational, and our CH_2O measurements on this day in conjunction with the 24-hour CMAQ model results at the surface are used to assess the level of agreement. This exercise is important since the 24-hour DNPH sampling results have been employed every 6th day over a number of years to collect averaged CH_2O levels at both Deer Park and Clinton, and these data have been used to infer decreasing yearly trends in CH_2O. Unfortunately Sept. 13 at Deer Park was the only day where the sampling system was operational during a P3 flight day.

The traces of Fig. 6 show the results of this comparison. In the top trace, we plot the P3 measurements for both CH_2O (blue points) and propene (red points) at the point of closest approach to the Deer Park sampling site for each of 3 circuits at the indicated local sampling times. The CH_2O measurements also include the total uncertainty (systematic plus random), and we indicate the sampling altitude. The 24-hour averaged DNPH measurements acquired by the TCEQ system at Deer Park are shown by the solid blue line spanning the 24-hour time period. The agreement in P3 propene measurements from the Wisthaler's group PTRMS instrument with the ground-based TCEQ auto GC measurements collocated with the DNPH sampling system indicate that the P3 and ground sampling site are in the same airmass for all 3 circuits. Without any further information it would be impossible to tell if the significantly elevated propene measured by the auto-GC sampler at around 4 am produces elevated CH_2O. Since there is no significant OH at night to initiate oxidation of propene to CH_2O, one would expect no corresponding CH_2O increase in the dark unless ozone reacts with propene in the dark to produce CH_2O. This would only occur if the elevated propene does not simultaneously occur with simultaneous large emissions of NO from flaring, which would titrate down the O_3.

It is interesting to note that the 24-hour CMAQ temporal profile of CH_2O at the Deer Park surface site shown in the lower trace of Fig. 6 (dashed blue line) indicates a large increase in calculated CH_2O at around 4 am. In fact, the CMAQ temporal CH_2O profile follows the measured propene profile. Since CMAQ employs an average emission inventory for each hour for a given season, the apparent coincidence in elevated calculated CH_2O and measured propene on. Sept. 13 in the early morning hours implies that early morning propene spikes at the surface at Deer Park should be a daily occurrence. Throughout the month of September in 2013 the hourly Deer Park auto-GC measurements in fact show such propene spikes on most days between the hours of 4 am and 7am, with typical levels in the 10-30 ppbv range and a maximum value of ~ 90 ppbv. This in turn would imply that elevated surface CH_2O at Deer Park should be a regular occurrence from fugitive emissions and subsequent reactions of O_3 with propene and perhaps ethene in the dark unless O_3 is simultaneously titrated by flares. This latter process, however, would directly release CH_2O (see Fig. 3).

Aside from the interesting time dependence and associated speculation just discussed, the 24-hour CMAQ surface modeled CH_2O at Deer Park shown in the lower trace of Fig. 6 can be used in conjunction with the P3 CH_2O observations to assess 24-hour DNPH results. As can be seen, the CMAQ model results at the surface at Deer Park agrees with the P3 measurements to within 205 pptv, which is even closer than our previous comparisons. Averaging the CMAQ CH_2O results over the 24-hour DNPH sampling period yields the 4.095 ± 1.9 ppbv value shown at the left on the Y-axis. Applying a small 205-pptv correction to match the CMAQ results with the 3

P3 measurements yields the 3.890 ± 1.9 ppb result shown with the Corr-CMAQ point. This value is in agreement with the averaged DNPH results (2.673 ppbv) within the precision of the CMAQ mean value. The difference is 31%. It is interesting to note that the DNPH value is in line with our averaged daily mean and median CH_2O values of 2.928 ± 0.382 ppbv, and 2.788 ± 0.481 ppbv, respectively, for the composite PBL shown in Fig. 5. **Based on these limited observations, the Deer Park DNPH sampling system should accurately reflect 24-hour integrated surface CH_2O levels at this site.**

Clearly more comparisons should be carried if the opportunities arise in the future. In particular, CH_2O measurements with our IR spectrometer located at the Deer Park and Clinton DNPH sites, sampling for at least 1-month each, would provide extremely valuable information. In addition to providing more substantial comparisons with DNPH results, such observations would help to address the nighttime questions just discussed.
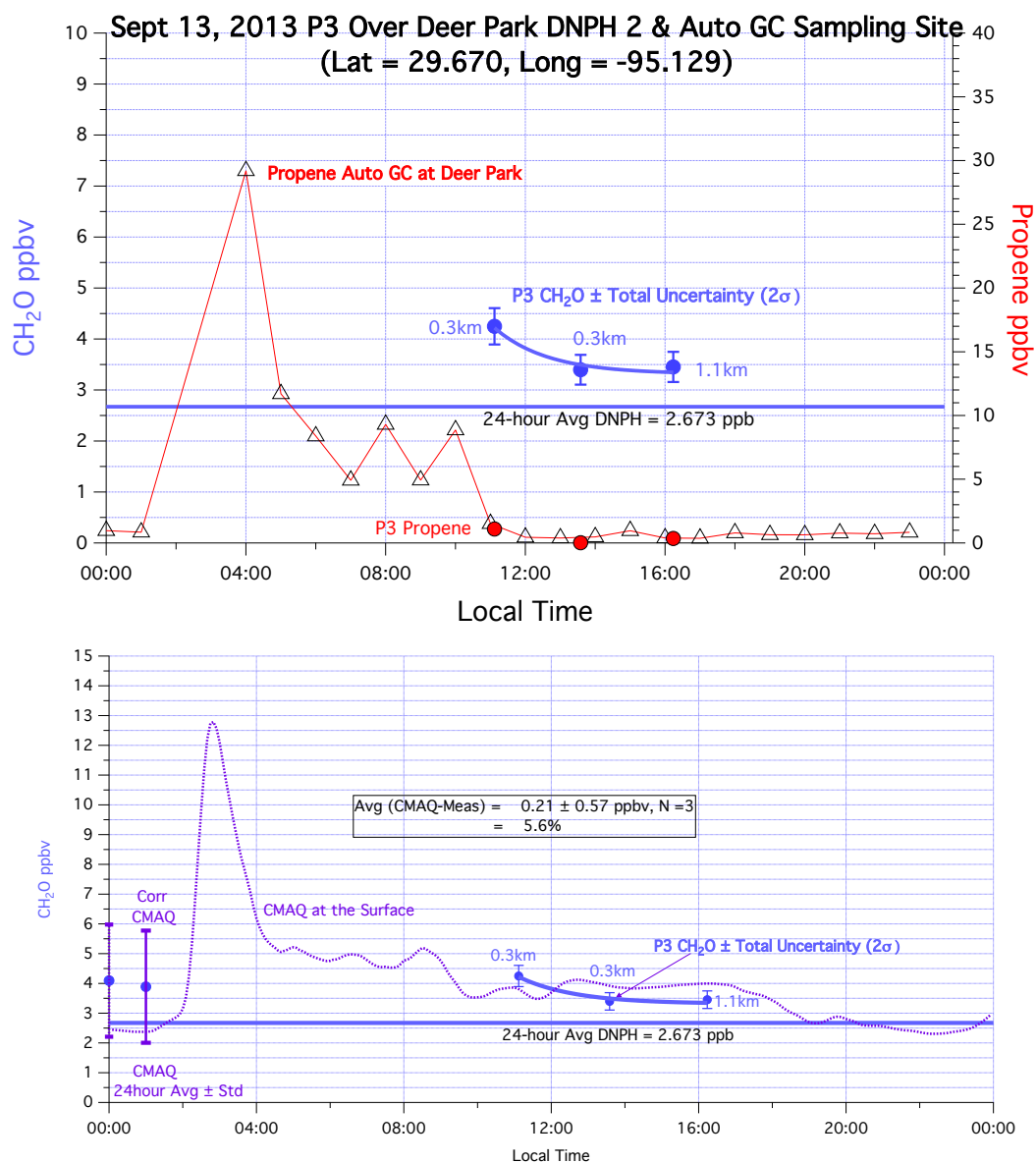

Figure 6: (Top trace) Comparisons of P3 propene measurements with the auto-GC measurements at Deer Park. (Bottom trace) Comparison of P3 measured CH_2O concentrations with CMAQ calculations at the surface of Deer Park and the 24-hour averaged DNPH results.

Data Collected
None.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
No problems encountered.

Goals and Anticipated Issues for the Succeeding Reporting Period
Improve emissions inventory (E) based on the following ratios for a new CMAQ simulation with process analysis:

Detailed Analysis of the Progress of the Task Order to Date
We don't anticipate delays in the completion of this project.

Submitted to AQRP by: Alan Fried
Principal Investigators: Alan Fried and Chris Loughner