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**	7/9/2015
REPORTING PERIOD	**From:** June 1, 2015 **To:** June 30, 2015	**REPORT #**	9

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

During the June reporting period we accomplished the following tasks: 1) prepared and presented at the University of Texas AQRP workshop in Austin a talk summarizing the progress and findings on our project to date; 2) developed and started to implement methods to identify 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 3) initiated efforts to run the CMAQ model in the Process Analysis mode to determine CH_2O source attribution over the entire Houston-Galveston-Brazoria Metropolitan Area.

Preliminary Analysis

Our June 18 workshop presentation highlighted the following major findings thus far:

a) The importance of direct CH_2O emission sources from petrochemical flares
b) The importance of photochemistry downwind of such sources in producing additional CH_2O and O_3
c) Support for the integrated 24-hour DNPH results at the Deer Park sampling site
d) The importance of early morning emissions of propene and potentially CH_2O near this sampling site. As discussed in both the presentation and in last month's report, the CMAQ modeled CH_2O at the surface at Deer Park followed the measured propene increase. As discussed, this implies 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. In his presentation, Fried further stressed the importance to further understand this behavior by carrying out high time resolution CH_2O measurements at Deer Park and potentially at other surface sites in the future.
e) The observation of distinctly different CH_2O measurement profiles between 2013 and earlier studies (2006 and 2001) where CH_2O >10-ppbv was frequently observed. In 2013 by contrast, with the exception of Sept. 25, CH_2O levels were mostly < 6-ppbv.

f) Despite large (CMAQ-Measurement) differences between 1-second observations and 5-minute model results, we obtained good daily agreement on average. Excluding Sept. 25, the average-median and average-average (CMAQ-Measurement) bias in the boundary layer were -309 ± 322 pptv, and -470 ± 306 pptv, respectively

g) A significant fraction of the elevated CH_2O and O_3 was found to be associated with well aged photochemically processed air.

Figure 1 below illustrates the major finding (g). Here we plot all the planetary boundary layer (PBL) 1-second CH_2O and O_3 data (Andy Weinheimer's NCAR chemiluminescence instrument) acquired on the NASA P3 aircraft during the entire September 2013 sampling period. The measurement points are colored and sized by the NO_x/NO_y ratio (from the same Weinheimer chemiluminescence instrument), with the larger points denoting the higher ratios.

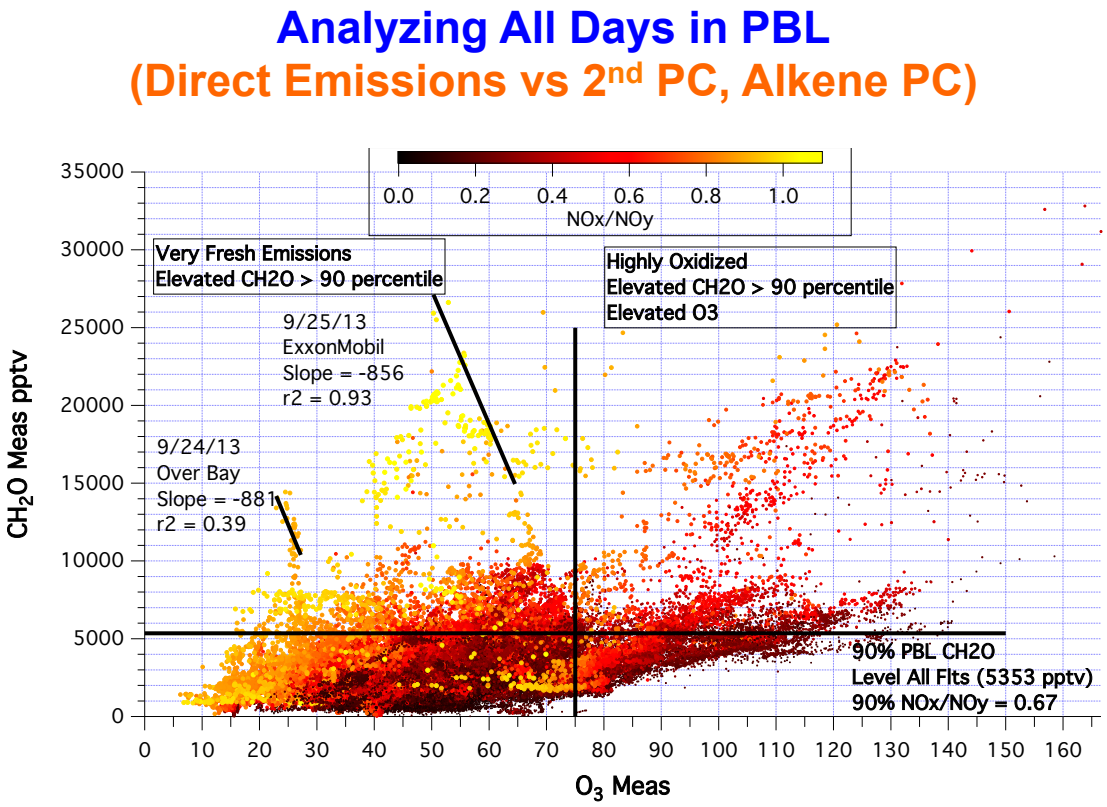

Figure 1: Fast 1-second correlations of all the CH_2O and O_3 data acquired in the PBL during the 9 DISCOVER-AQ flights over the Houston-Galveston-Brazoria Metropolitan Area for the entire month of September, 2013.

The NO_x/NO_y ratio is one of many indicators that reflect the degree of photochemical processing. Fresh emission plumes, such as from the two flaring plumes highlighted by the solid regression lines in Fig. 1 have ratios in the 0.9 to 1.0 range, where nearly all of the nitrogen-oxides are in the form of NO_x ($NO+NO_2$). As the air mass ages, the NO_x undergoes oxidation to form species such as HNO_3, PAN, alkyl nitrates and other species. In addition, in fresh flaring emissions, O_3 is titrated by the emitted NO, resulting in a highly anti-correlated (negative) CH_2O-O_3 slope. The two highlighted regression slopes yield CH_2O-O_3 slopes of -856 pptv/ppbv and -881 pptv/ppbv. The time series showing the CH_2O, O_3, propene, CO and NO_x/NO_y profiles over the ExxonMobil complex during the 1st circuit of September 25 are shown in Fig. 2. This

same figure, which was presented in last month's report and discussed at great length during the workshop, is repeated here for completeness.

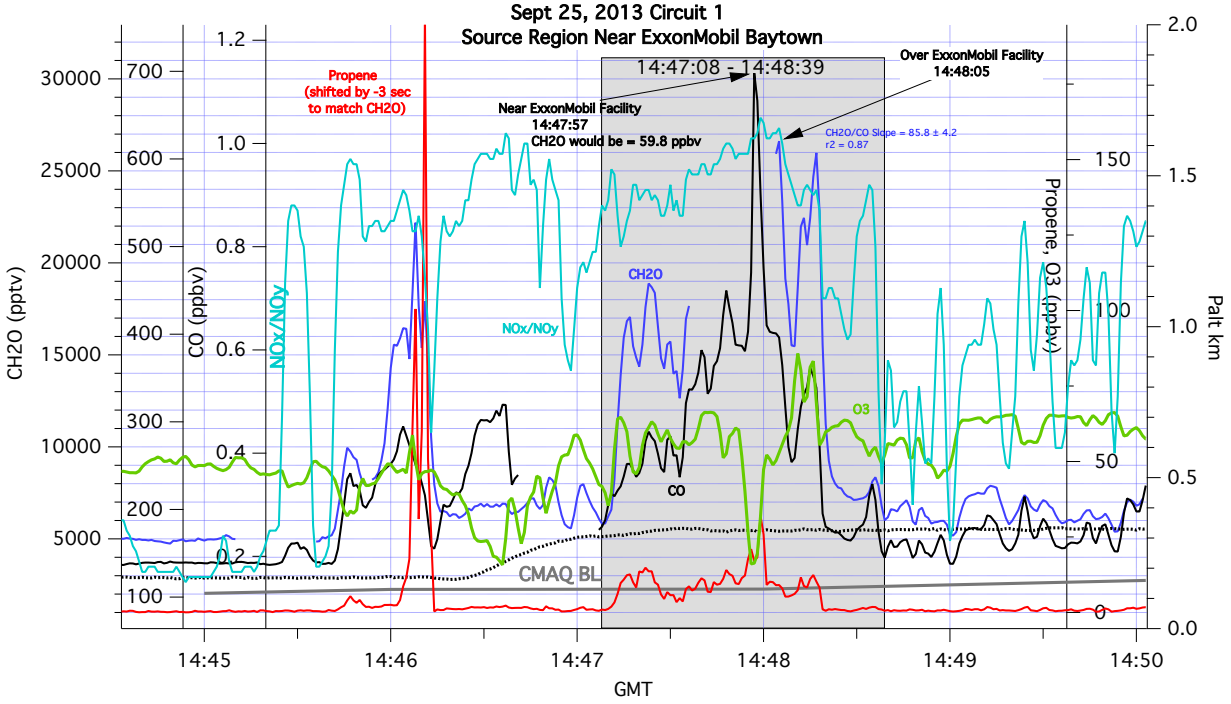

Figure 2: Time series plot of CH_2O, CO, O_3, propene, and NO_x/NO_y ratios during the 1st Circuit of Sept. 25, 2013 near the ExxonMobil Baytown complex**.**

For reference, Fig. 1 also shows the 75-ppbv 8-hour O_3 limit by the vertical line as well as the 90% for all the PBL CH_2O data as a solid horizontal line. A few observations are immediately evident in examining Fig. 1: 1) the very fresh CH_2O emissions, which yield very high levels up to ~ 25-ppbv in the upper left *quadrant* are mostly associated with high NO_x/NO_y ratios and low O_3 values less than 75-ppbv; 2) the predominance of the CH_2O data at and below the 90% level of 5.3-ppbv are mostly associated with well-aged air, with a 90% NO_x/NO_y ratio of 0.67 and median value of 0.29; 3) nearly all of the very high O_3 data (> 75-ppbv) and high CH_2O data (> 90% level line) in the upper right *quadrant* are associated with well aged highly oxidized conditions; 4) the CH_2O levels for this quadrant, which approach 33-ppbv, exceed the observed direct emission levels; and 5) data in the lower right *quadrant*, where CH_2O levels are less than the 90% line but O_3 is > 75-ppbv, are also mostly associated with well-aged highly oxidized air. Finally, overall Fig. 1 suggests that the majority of the 1-second PBL CH_2O measurements over the Houston-Galveston-Brazoria Metropolitan Area during the month of September in 2013 are associated with well-aged highly oxidized conditions. Although highly suggestive that 2nd CH_2O production dominates the Houston-Galveston-Brazoria Metropolitan Area, it must be noted that Fig. 1 only covers ~ 1/3 of the month of September (9 flight days out of 30), about ~ 1/3 of the hours in each sampling day (~ 8 flight hours out of 24), only covers 1 month of the year, and may not cover all of the direct emission sources despite flight patterns designed to sample the largest VOC emission sources. To address these shortcomings and provide additional support regarding the relative importance of 2nd photochemical CH_2O sources, we will be employing the CMAQ model in the Process Analysis mode to determine CH_2O source attribution over the entire Houston-Galveston-Brazoria Metropolitan Area, initially for the month of September in 2013 and if feasible for the entire year. This effort is currently being initiated, and we hope to have results in next month's report.

As stated in last month's report, we are currently analyzing all boundary layer P3 time periods to identify similar events as the September 25 flaring event. In this effort, we are tabulating O_3-CO-CH_2O slopes and correlation coefficients along with NO_x/NO_y ratios. We had planned on finishing this analysis by the time of this report, however, the computer coding to automate the search has taken longer than planned and the results are not yet complete. Once all the interesting flaring events have been identified we will follow up with CMAQ back trajectories to pinpoint the source regions.

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
Run CMAQ simulations with process analysis for source attribution and in addition finish up the identification of all petrochemical-flaring events.

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

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