

**Appendix DD**  
**Summary of Analyses of Enhanced Industry-Sponsored**  
**Monitoring (EISM) Data**  
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**Introduction**

In June 2003, seven new automated gas chromatograph (“Auto-GC”) monitors were brought on-line in the Houston-Galveston area. Together with the existing TCEQ Auto-GCs located on Clinton Drive and in Channelview, this brings to ten the number of Auto-GCs whose data were analyzed for this project<sup>1</sup>. As with the existing Auto-GCs, data is collected for the current PAMS target species list, which contains approximately 55 unique VOCs.

This report provides a summary of analyses. More detailed information, including a map and list of monitors, can be found at the following web site:

[ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Workshops/TCEO\\_Staff\\_Presentation/20040219-Analysis\\_of\\_HG\\_Enhanced\\_Industry\\_Sponsored\\_Monitoring\\_Data-JohnJolly.pdf](ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Workshops/TCEO_Staff_Presentation/20040219-Analysis_of_HG_Enhanced_Industry_Sponsored_Monitoring_Data-JohnJolly.pdf)

**Analyses**

Eight types of analyses have been performed on the data retrieved from these monitors. These include:

- Morning median total VOC concentration, by monitor;
- Morning median total VOC reactivity, by monitor;
- Morning median reactivity, by compound and by monitor;
- Median contribution to total VOC reactivity by VOC class and by monitor, for all hours and for high-reactivity hours;
- Geometric mean of selected compounds, and of total reactivity-weighted concentration, by wind direction at each monitor;
- Source attribution analysis of propylene in Ship Channel;
- Analysis of selected high-ozone episodes, and;
- Median reactivity-weighted concentration of propylene and ethylene by hour and by monitor.

All of these analyses have been performed regularly (i.e. with each addition of new and/or validated data) except for the first and last ones.

These analyses have included all of the data available for each monitor, i.e. from the monitor start date until approximately one month prior to the analysis date. Data for each monitor becomes available for analysis before they are validated; validation typically

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<sup>1</sup> The TCEQ Auto-GC at Deer Park (CAMS 35) experienced technical difficulties in much of 2003; its data are being reprocessed and revalidated, and were not ready at the time of this report.

takes at least two more months. Therefore, all of the analyses described here include both validated and unvalidated data.

Here is a brief description summarizing the results of each analysis, using data from June 2003 through January 2004. Texas City CAMS 620 is excluded from all analysis until concerns about the validity of its data can be eliminated.

- Morning median total VOC reactivity, by monitor – this analysis shows that the four monitors located closest to the ship channel (Lynchburg C1015, Channelview C15, Clinton C403, and HRM 3) have considerably higher median morning reactivity than do the other five monitors.
- Morning median reactivity, by compound and by monitor – this analysis shows that for the Ship Channel monitors, ethylene and propylene have the greatest morning reactivity-weighted concentrations, by median value, of any VOC species. Of the HRVOCs, and the highest median alkane species, Channelview, Lynchburg, or Clinton had the highest median values, except for isopentane, where the highest morning median value was observed at Texas City. For the Brazoria county monitors, overall reactivity-weighted concentrations were usually much less than the Ship Channel ones. Mustang Bayou C619 usually had the highest median concentration of the three Brazoria monitors; however, isoprene was higher at Lake Jackson C1016 and Sweeny C618 than at Mustang Bayou.
- Median contribution to total VOC reactivity by VOC class and by monitor, for all hours and for high-reactivity hours – here the 55 VOC species were grouped into 17 classes. In general ethylene and propylene (each one forms its own class) were the biggest contributors to VOC reactivity. However, some distinctions were seen among the monitors. At four of the monitors – Lynchburg, Wallisville C617, Lake Jackson, and Sweeny – ethylene and/or propylene contributed much more to total reactivity during high-reactivity hours than when all hours were examined. At HRM 3 and Channelview, the contribution of ethylene and/or propylene to total reactivity in high-reactivity hours increased modestly compared to when all hours were examined. At Clinton, almost no change was observed in the contribution of the different VOC classes between high-reactivity hours and all hours. Finally, Mustang Bayou was unique among the ten Auto-GCs – it showed greater contribution by alkanes during high-reactivity hours than when all hours were examined.
- Wind directional analyses at Ship Channel monitors – these were done for ethylene and propylene at the five monitors, and for benzene and styrene at four of the five monitors (Clinton was excluded). For ethylene, the greatest peak is at bin 160 for HRM 3, with a geometric mean of almost 25 ppbC. At Lynchburg, there is a peak at bins 170-180 that is greater than 20 ppbC. At Wallisville, there is a peak of about 13 ppbC centered at bin 220. All other bin values are 11 ppbC or less. For benzene, Lynchburg exhibited strong peaks at 10-20 degrees and at

220, much higher than those observed by the other monitors. The peaks at 10-20 degrees point to a couple of barge cleaning facilities up the San Jacinto river, and the peak at 220 points to the east Deer Park area. For styrene, a peak at 20 degrees at Lynchburg was much higher than any other peak at Lynchburg or at the other monitors. Also, at Lynchburg only, xylenes data were compiled and plotted in the same manner, and a strong peak was once again observed at 20 degrees. Discussion regarding propylene is found in the next paragraph.

- Wind directional analyses at Brazoria County monitors – these were done for ethylene, propylene, 1,3-butadiene, and butenes at the three monitors. Ethylene or propylene had the highest peaks at all three monitors. Peaks pointed to both local sources (e.g. Lake Jackson had a peak pointing to the Dow Freeport plant) and also to the north of all three monitors, where it hasn't been determined if these are local sources or emissions from the Ship Channel. Geometric means, even of the highest peaks, were much less than those observed at the Ship Channel.
- Source attribution analysis of propylene in Ship Channel – in this analysis, geometric means of propylene concentrations by wind bin at the four monitors were combined with maps of propylene point sources, to determine the sources upwind of the highest concentrations. For the three monitors with the highest peak concentrations, maps revealed that each monitor's peak pointed to the Battleground Road area, where a cluster of two large sources is located. This cluster ranges from 3.9 to 14 km distance to the monitors; there are numerous other clusters in the Ship Channel area with propylene emissions that are large. Many of these clusters are located closer to the monitors than is Battleground Road. This suggests that emissions from one or more of these two sources at Battleground Road are substantially underreported relative to the other sources in the area.
- Additional analysis of propylene at Lynchburg Bin 190 – wind bin 190 (which includes winds from 185-195 compass degrees) at Lynchburg had a geometric mean propylene concentration of about 80 ppbC, much higher than any other peak at that or any other monitor. This bin points to the Battleground Road industrial cluster, 3.9 km away. The data points that fell into this bin were examined in greater detail. It was found that 80% of the values were 30 ppbC or greater, and 63% of the values were 60 ppbC or greater. This suggests that high values are a regular occurrence at this bin, and may be due to regular elevated emissions. Also, it was found that high values seemed to occur regularly throughout the monitoring period, when wind blew from this direction. Finally, the median ambient propylene:Nox ratio was calculated to be 5.8 to 1, whereas the same ratio for emissions sources located in the bin was 1.8:1, suggesting that the emission inventory for sources in the bin is underestimated by over three-fold.
- Analysis of selected high-ozone episodes – this was an attempt to analyze VOC data from one or more of the new Auto-GCs during a period when ozone was elevated, to see if the new VOC data could help facilitate understanding of the

elevated ozone. For the presentation whose link is listed in the first paragraph of this paper, a very high ozone episode (on 10/23/2003) was analyzed in conjunction with the Auto-GC data. Here, VOC data were plotted together with 5-minute ozone data at the two Auto-GCs – Clinton and HRM 3 – where peak one-hour ozone exceeded 125 ppb. Though the cause(s) of this event have not been determined, it could be seen that a very reactive air mass – whose reactivity was fueled by several alkanes as well as ethylene and propylene – passed by Clinton at approximately the same time that ozone concentration was increasing dramatically. (This case study was supplemented by aircraft data, as can be seen in the presentation.)

- Median reactivity-weighted concentration of propylene and ethylene by hour and by monitor – this analysis was done regularly up through October 2003, when it included data from June through September. It revealed that at all ten monitors, concentrations of propylene are lower during midday (hours 1200-1659) than at other hours, which is expected given that mixing height is highest, on average, during midday. Given that this analysis seemed to reveal nothing significant beyond that, it was discontinued following the 10/20/2003 presentation.

### **Summary**

The analyses performed using the new Auto-GC data after just the first six months of operation reveal important findings. First, data from the Lynchburg C1015 monitor suggest that it is unique among the Ship Channel monitors for several reasons. It sees VOC concentrations, and reactivity-weighted concentrations, that in many cases well exceed those of all other monitors. Based on data thus far, its location enables it to “observe” propylene emissions from a geographically small source cluster whose emissions appear to vastly exceed their reported quantities, and who may be the dominant source of propylene in the area. This may provide additional insight into sources of high reactivity in the area.

As well, the increased density of the Ship Channel Auto-GC monitoring network, afforded by the addition of the new monitors, helps confirm earlier analyses suggesting that VOC reactivity in the area is very high. The new Auto-GC monitoring network in Brazoria County suggests that there is a quantifiable, substantial difference between air mass reactivity there and the Ship Channel.