

Attachement 5

Analysis of TexAQS Airborne Canisters

3.1 Analysis of TexAQS airborne canisters

Hydrocarbon canisters collected by the Baylor Twin Otter, the Department of Energy's G-1, and the NCAR/NOAA Electra on flights in and around the HGA have been studied. To simplify the analysis of this comprehensive data set only common VOCs, those compounds found in each program's hydrocarbon speciation, were evaluated (See Figure 3-14). Due to time limitations the alkanes, aromatics, and other species were not reviewed in the depth the other compounds received. This analysis did not consider the altitude or time of the sample collection, nor if the canister was taken in an industrial plume.

To begin this process, the 666 canisters collected in 2000 were plotted on maps to determine their location. The most reactive canisters were observed in or downwind of the industrial regions of Houston such as the Ship Channel, Bayport, Baytown, Texas City and Clute/Freepport areas. The canisters collected in other areas had substantially less reactivity. Figure 3-1 depicts the OH and Maximum Incremental Reactivities (MIR) of the airborne canisters. The yellow, orange, and red symbols show canisters with "high" reactivity, above 10 in OH s^{-1} and above 166 in MIR. These thresholds capture the top 10% of reactive samples collected in the HGA. MIR values were calculated by converting Carter's 05/08/2000 MIR mass values (Carter, W.P., 2000) into molar values and then multiplying by the measured ppbv concentration.

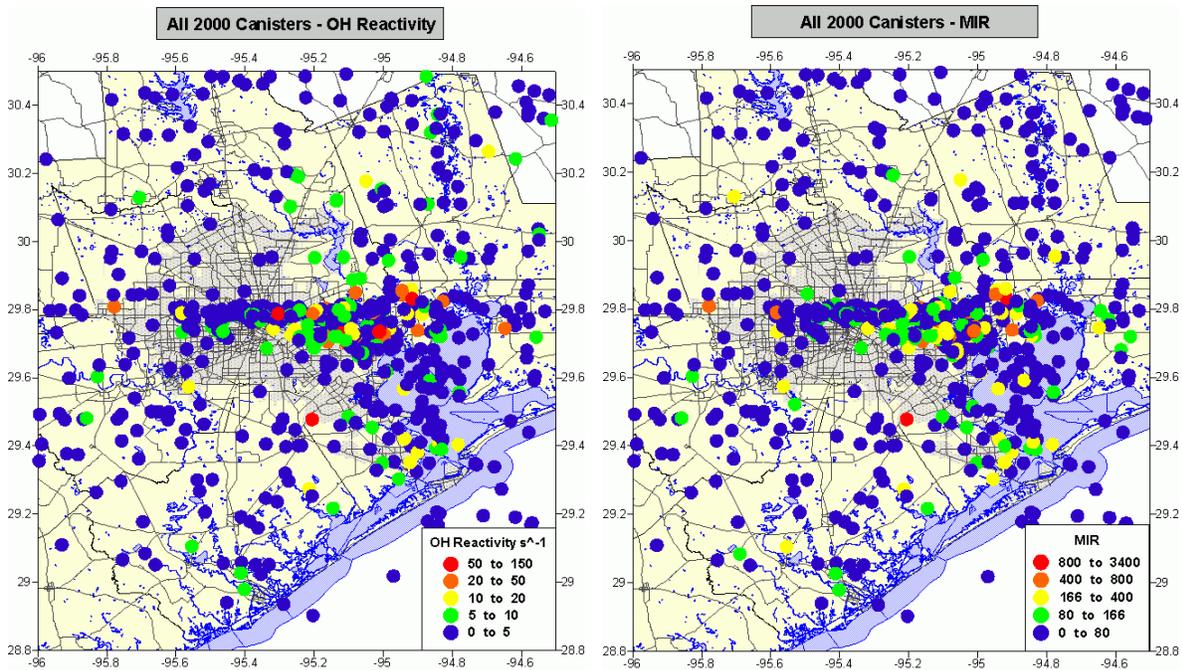


Figure 3-1

The early results of this study are presented below. Figure 3-2 shows the mean percentage each compound or compound group comprises of the total common OH and MIR reactivity in the Houston Industrial areas of the Ship Channel, Channelview, Baytown, Bayport, Mont Belvieu, Texas City, and the Clute/Freeport areas. Ethylene and propylene in both scales comprise approximately 35 percent of the common total reactivity while the butenes, isoprene, alkanes, and butanes also contribute significantly.

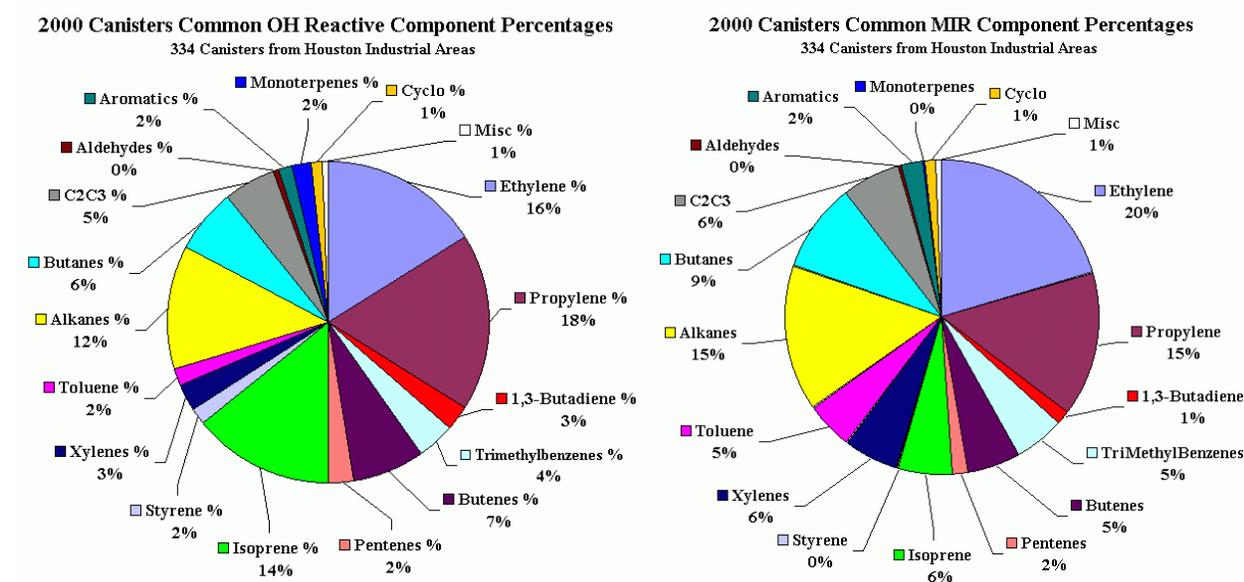


Figure 3-2

While Figure 3-2 displays the average percentages of the VOCs in the aircraft canisters, each canister profile may vary substantially. Figures 3-3 through 3-11 exhibit the common OH reactivity of the canisters collected during each day during the modeling period. Creating bar charts of each canister not only yielded important speciation profiles but allowed for comparison to the photochemical model results. The OH reactivity scale does change from day to day but the order of the compounds remains the same, i.e., ethylene and propylene will always be the same colors and at the bottom of the bar. Also, sample location can influence reactivity and canister composition.

One particular canister on August 30, 2000 had such high OH reactivity that the other canisters were dwarfed in comparison. For that particular day the bar graphs are presented on two pages; the second page allows the highly reactive canister to run over the top of the graph so the reader can see the detail in each of the other canisters. This canister was scrutinized in much more detail than the other canisters during the modeling period due to its extensive amount of reactivity and proximity to the highest surface recorded ozone concentration for the day at the HRM-8 monitor (C608). Figure 3-12 shows the location of this canister (eastern red dot), the back trajectory associated with it (other red dots created using aloft wind data), monitors (orange triangles) and nearby point sources (open black circles). The green rectangle denotes an area of possible source influence based on the wind direction and wind speeds observed in the morning hours. Seven of the 26 large point sources that were modified in the model by setting their HRVOC emissions equal to their NO_x emissions were found along the back trajectory of this

canister. A HRVOC to NO_Y ratio was calculated using the canister VOCs and onboard NO_Y instrument values, and found to be approximately 1.5:1.0. A photochemical modeling sensitivity run was conducted using the HRVOC to NO_Y ratio for this day (i.e. increasing the HRVOC emissions of the seven large sources by 1.5). These model results are discussed in Section 2.

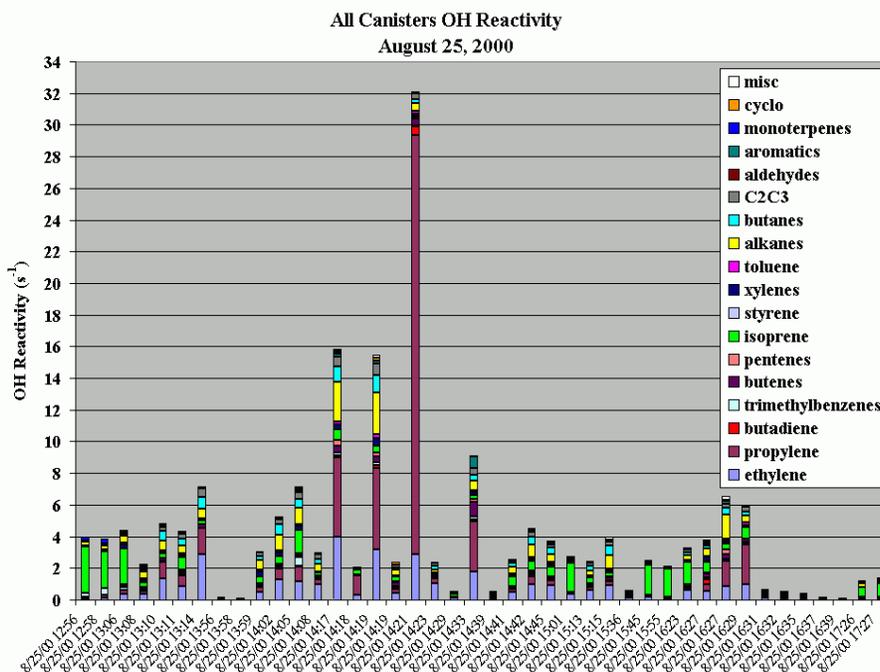


Figure 3-3

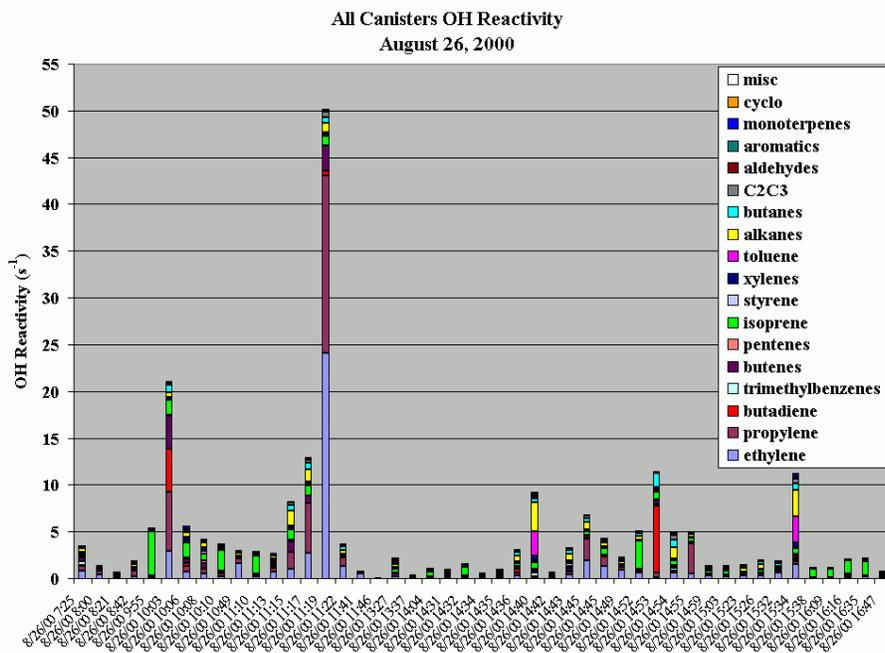


Figure 3-4

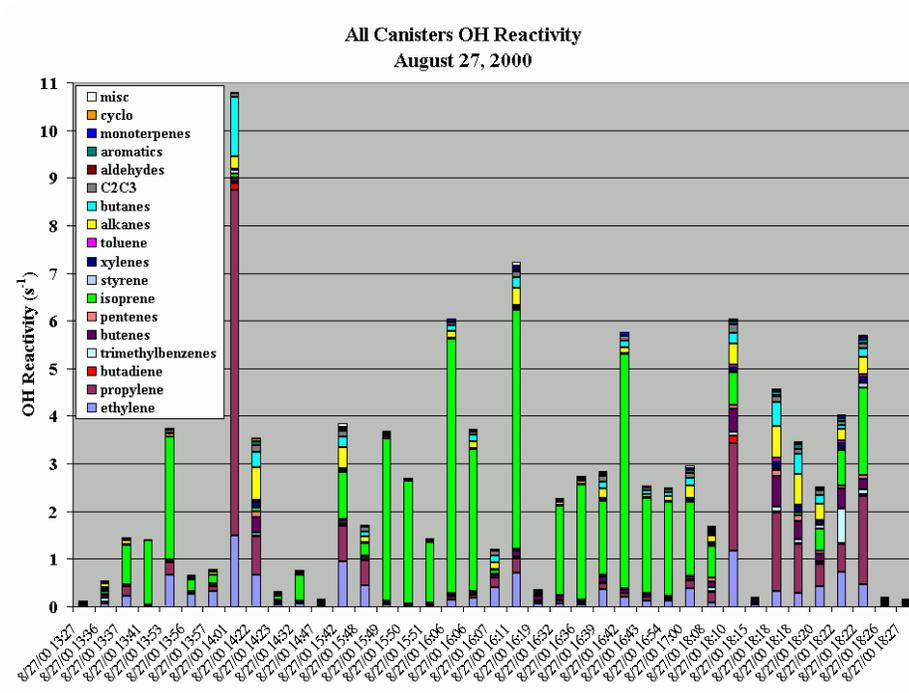


Figure 3-5

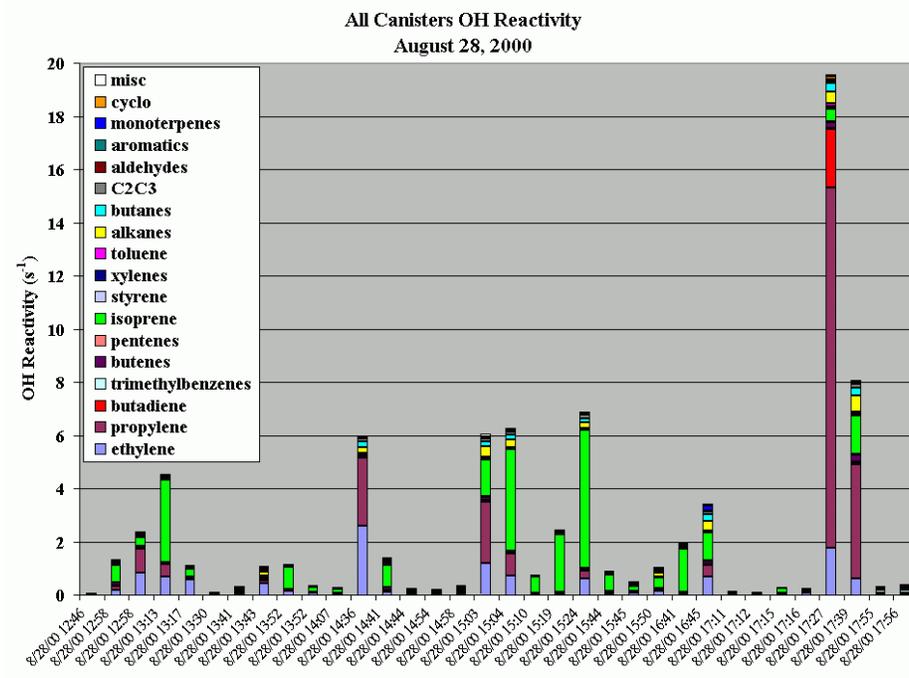


Figure 3-6

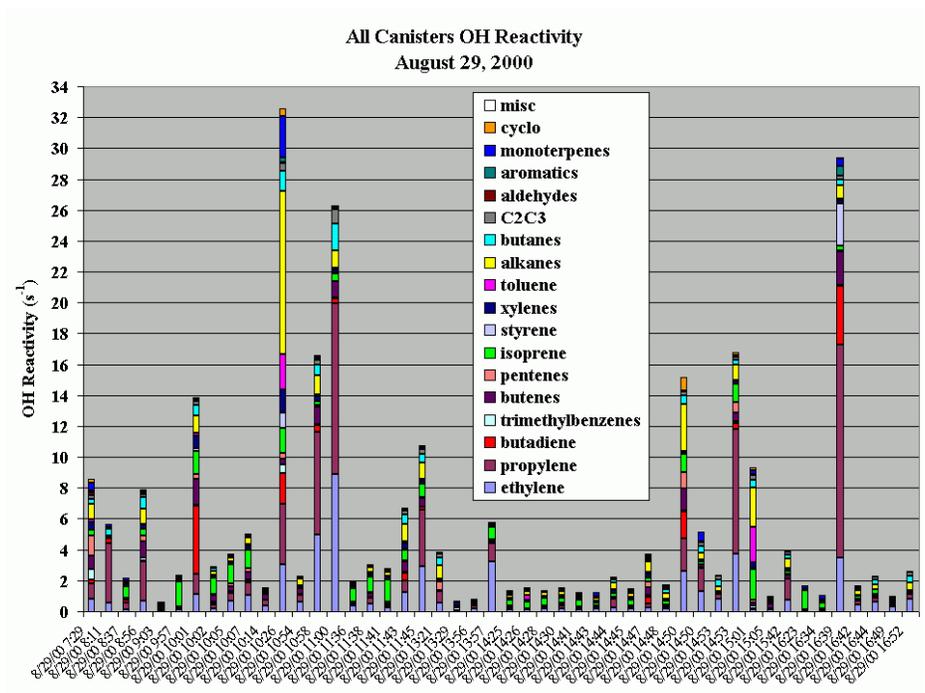


Figure 3-7

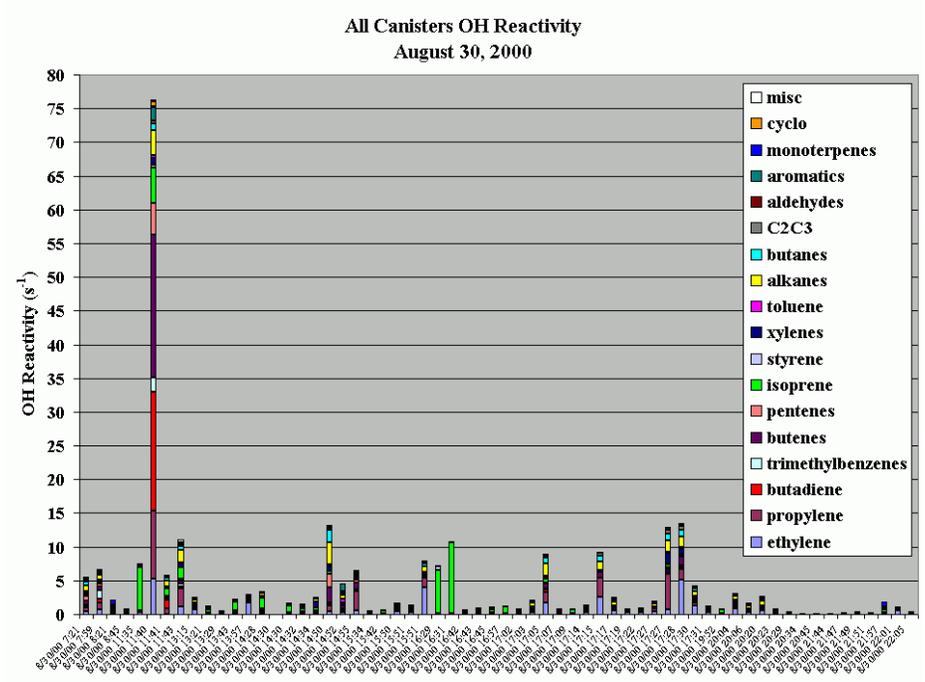


Figure 3-8

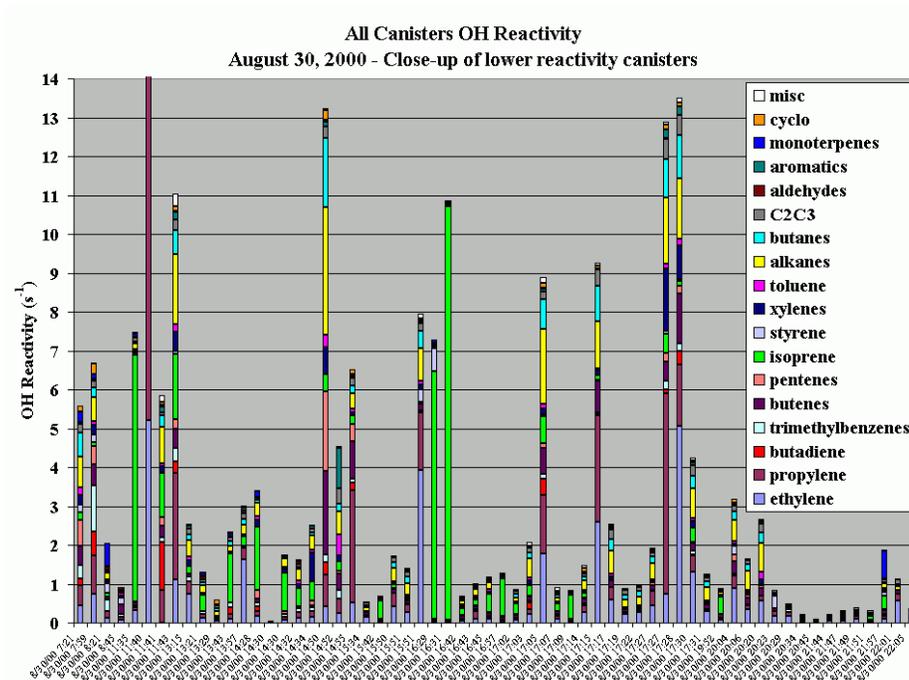


Figure 3-9

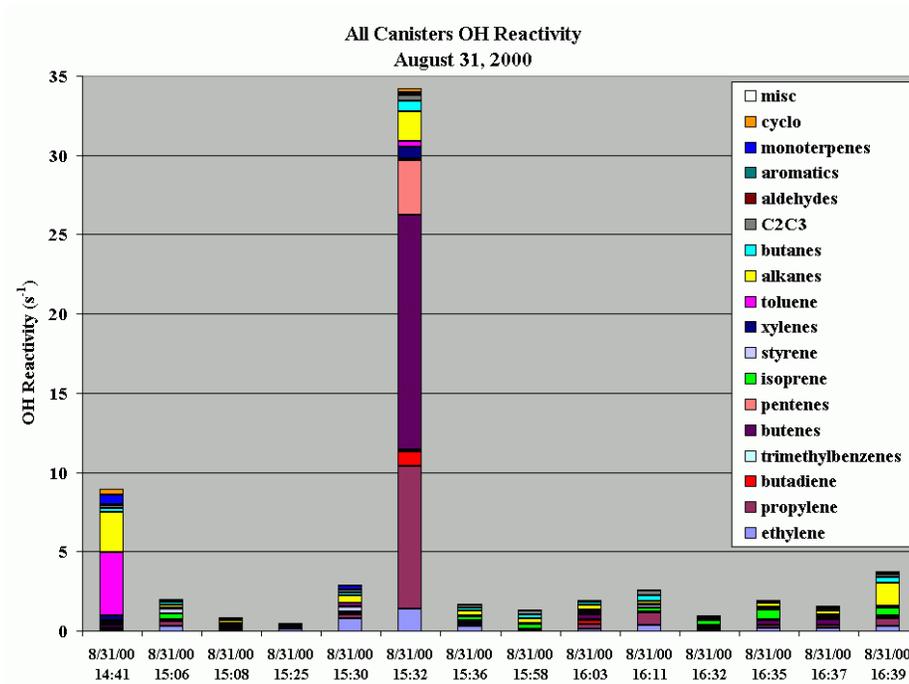


Figure 3-10

All Canisters OH Reactivity
September 1, 2000

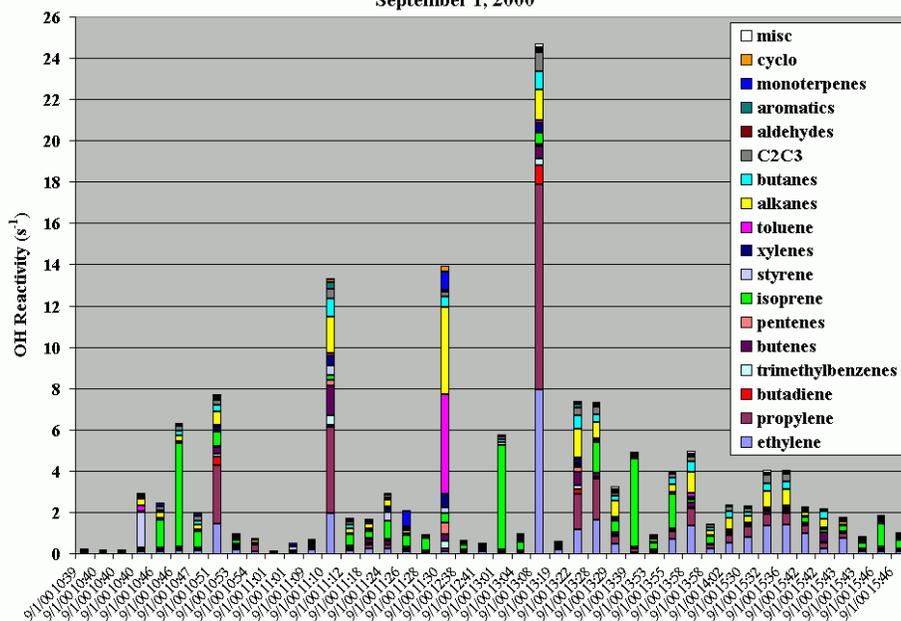


Figure 3-11

Back Trajectory for the NCAR canister collected at 11:40:58 on 8/30/00

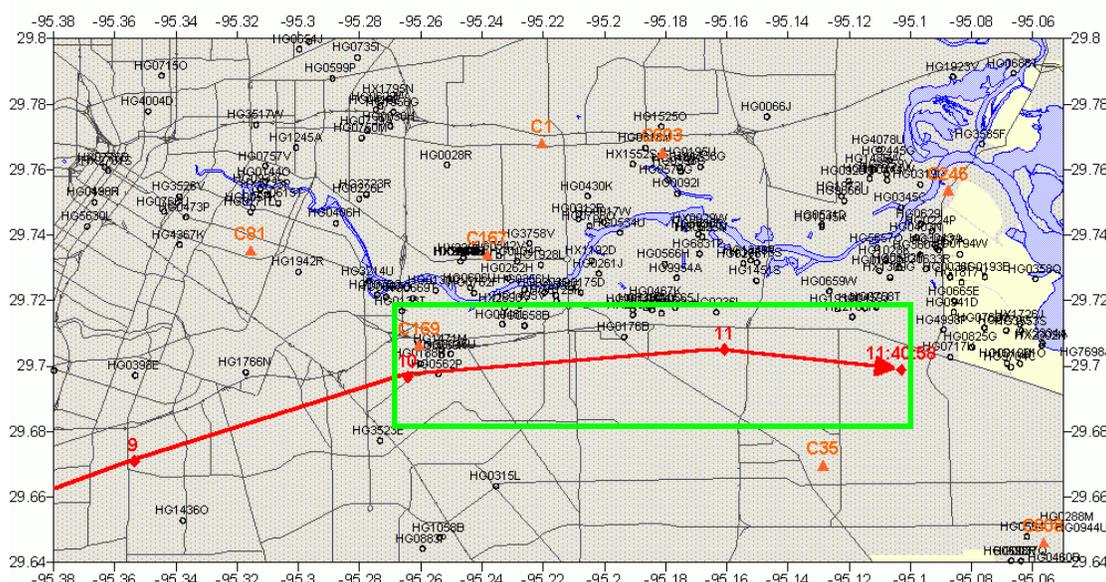


Figure 3-12

Figure 3-13 contains a bar chart of the top 25 common OH reactive canisters. As this chart shows, high reactivity was observed over many days and hours during the sampling period. This finding suggests that high reactivity is a routine occurrence rather than individual emission events. Figure 3-13 also shows ethylene and propylene among butenes and other highly reactive compounds comprise a large percentage of the total common OH reactivity in most canisters. However, the top two reactive canisters contain significant amounts of lower reactive compounds such as alkanes and toluene. During the next year, TCEQ will continue studying the less reactive compounds, especially the impact of alkanes, aromatics, butanes, and other compounds. Figure 3-14 is a list of compound groups and species analyzed. This study will attempt to answer whether large quantities of less reactive VOCs contribute to high ozone levels. This question may be difficult to evaluate because less reactive VOCs might form ozone at distances from the Houston industrial areas, outside the current monitoring network.

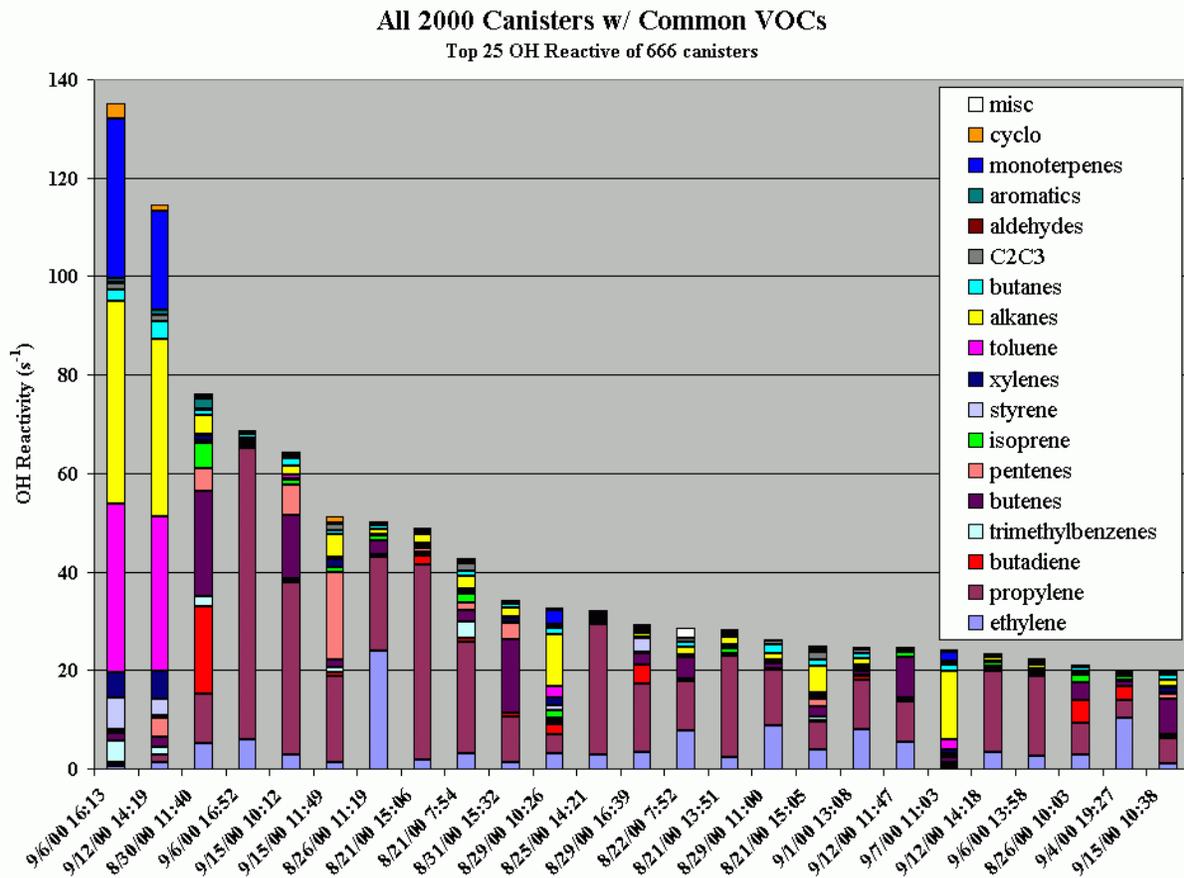


Figure 3-13

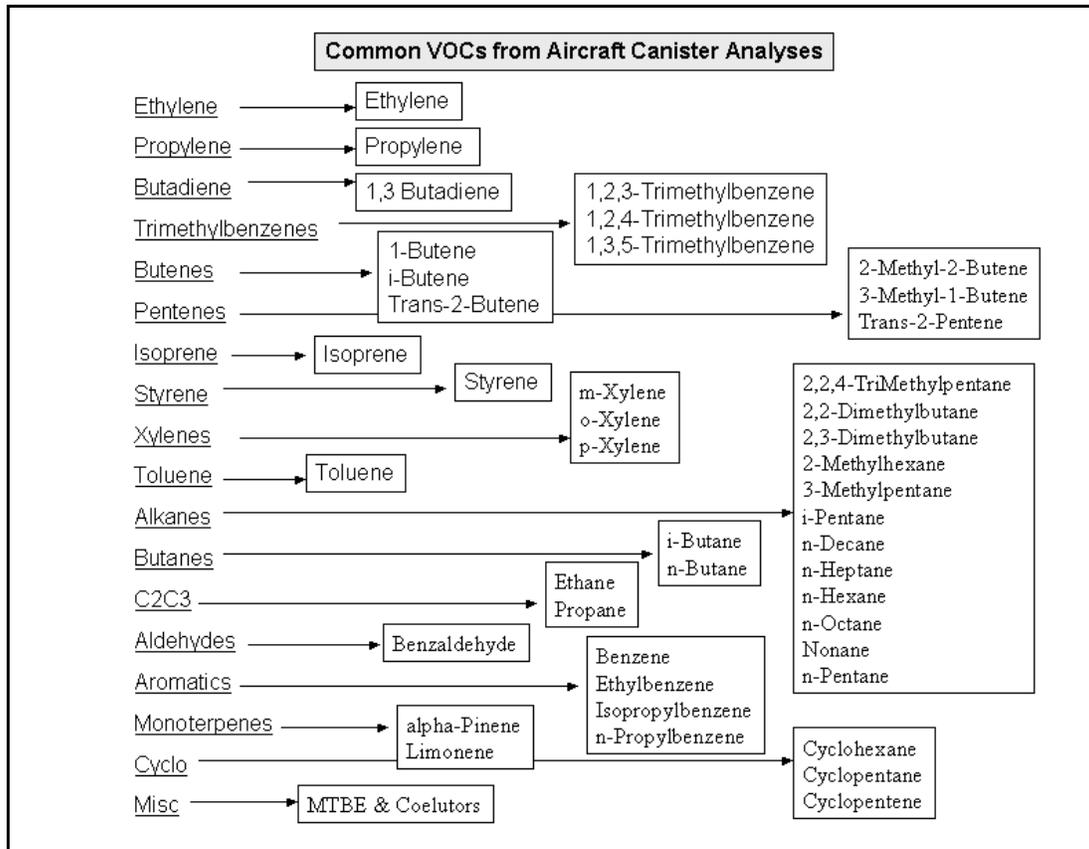


Figure 3-14

Canisters from 2000 and 2001 were compared to determine if there were any observed differences. The purpose of this exercise was to address concerns that the 2000 study period was dissimilar to other periods. The results of the canister analysis for 2000 and 2001 indicate the within-year variability in composition is greater than or equal to the between-year variability.

Results from Baylor's 2001 flight season using a special olefins instrument were received in early October 2002. An initial analysis of this data corroborates other scientific results that there is significantly more propylene and other olefins in the ambient air than reported in the annual emissions inventory. The TCEQ plans to study this unique data further and provide updated results for the Mid-Course Review.