ENVIRON

MEMORANDUM

To: Saffet Tanrikulu, Phil Martien, Steve Soong
BA MAC

From: Chris Emery, Ed Tai

Date: April 13, 2004

Subject: CAMx model performance for speciated and total VOC for July/August 2000

This technical memorandum provides plots comparing VOC measurements and CAMx predictions for the July/August 2000 episode in the Bay Area, Sacramento Valley, and San Joaquin Valley. A preliminary analysis was completed in January and reported at the February 10 MAC meeting. At that time, several issues were raised concerning the data quality and the need to present the distribution of total VOC as CB-IV species in absolute terms rather than in relative terms. A March 11 revision was submitted to the MAC that addressed these issues. This memorandum further addresses certain comments from the ARB and MAC on the March 11 memo, and adds an analysis of morning VOC:NOx ratios.

Approach

The VOC measurements were taken from the CCOS air quality database that we obtained from Greg O'Brien at ARB in the fall of 2003. Paul Allen at ARB also supplied a hydrocarbon "species key" that provides molecular weights, CB-IV carbon numbers, and a mapping of the several hundred individual species listed in the database to equivalent CB-IV and SAPRC99 compounds. We independently verified the CB-IV species mapping. Two sets of measurements were provided: a set of 3-hour lab-analyzed canister data from several sites in the CCOS study area, and a set of 1-hour field-calibrated GC-MS Saturn instrument data from three sites. Both sets of data were prepared and evaluated for this analysis. Our current information suggests that the CCOS air quality database we received from ARB does not include any data from PAMS sites, which utilize auto-GC instruments.

Note that the 1-hour GC-MS data provide many more samples, with many more species reported per sample, relative to the 3-hour dataset which exhibited a paucity of canister samples and species. We therefore believe that the 1-hour data provide a much more robust source of VOC measurements. In the analyses described below, a concerted effort was made to ensure that each sample provided adequate information from which to build CB-IV species concentrations. Determining which samples possessed sufficient information for the CB-IV build-up was relatively straightforward because the samples tended to either result in expected concentration levels consistent among samples at other sites, or they led to near-zero concentration totals. Because of this, we were able to select a minimum compound count criteria to accept or reject a given CB-IV measurement sample. Many samples (primarily from 3-hour canisters) were disregarded due to lack of data. Unfortunately, this fact rendered our earlier preliminary VOC performance analyses invalid.

It should be noted that the chemical lumping mechanisms implemented within air quality models, such as SAPRC99 and CB-IV, are not designed to represent the details of VOC chemistry for individual compounds such as those reported by field sampling. For example, compounds with very different reactivities are represented in CBIV chemistry based on classes of similar carbon bond structures, and are thus treated with representative reactivities for each class. While the reader should keep this in mind, it is nevertheless necessary to compare model results against similarly lumped VOC measurements to provide a general assessment of the model's emissions and chemistry. Special attention can be focused on a few VOC compounds that are treated individually in the model, such as isoprene and formaldehyde, which are important precursors of radicals. However, many samples in the CCOS dataset did not include sufficient measurements of these species.

The VOC predictions were derived using CAMx v4.03 in what we have labeled as "Run 8". Meteorological data came from Steve Soong's MM5 run labeled "LSMlandz0"; this was the run that Steve states performed better in the central valley but slightly worse in the Bay Area. Emissions data came from the BAAQMD-processed "a7" series. These files were downloaded on October 2, 2003 from the Alpine FTP site. They do not include the modified on-road mobile and biogenic emissions based on RAMS-observation hybrid temperatures developed by the District; nor do they include the latest updates to the area source inventory made by the ARB in January. The specific Alpine file names used to develop version "a7" emissions are listed below:

CCAQS_JULY2000_AR_V091203ship_R001_CBIVV03_CAMX_MODELFILES.tar
CCAQS_JULY2000_BI_revmet_V091703_R002_CBIVV03_CAMX_MODELFILES.tar
CCAQS_JULY2000_ELEV_V092703_R001_CBIVV03_CAMX_MODELFILES.tar.gz
CCAQS_JULY2000_FIRES_V100203_R001_CBIVV03_CAMX_MODELFILES.tar.gz
CCAQS_JULY2000_MV_revmet_V042903_R001_CBIVV03_CAMX_MODELFILES.tar.gz

The initial/boundary condition files in CAMx "Run 8" were ENVIRON's standard "fire-influenced" set. All other inputs remain consistent with previous CAMx runs performed for the District.

On the following pages we provide plots of measured and simulated VOC concentrations for sites and periods at which sufficient data were available. Total VOC and CB-IV compounds (ppbC) are shown for the 6-9 AM period. The hours of 6-9 AM were chosen because this period should best represent primary VOC emissions in the data and in the model, as it coincides with peak commute hours, low mixing rates, and zero to low reactive decay. Data from 1-hour GC-MS sites were averaged over the 6-9 AM period. The 3-hour canister samples directly coincided with the 6-9 AM period.

Results from three areas are shown: the San Francisco Bay Area (SFBA), the Sacramento

Valley (SAC), and the San Joaquin Valley (SJV). For sites in the SFBA, the comparisons between observations and predictions focus on the morning of July 31; however, 6-9 AM averages of 1-hour GC-MS data from the Sunol site were calculated over July 30 – August 1 for comparison. Averaging over multiple days of the episode helps to maximize the robustness of the comparison (i.e., it removes the influence of a few questionable samples, unimportant day-to-day variations, etc.). Multi-day averages were not calculated from SFBA 3-hour canister data due to insufficient data to develop reliable numbers. For sites in the Sacramento (SAC) and San Joaquin (SJV) valleys, the comparisons between observations and predictions focus on the morning of August 1. Averages over multiple days were not calculated for any SAC and SJV sites due to insufficient data.

Evaluation of Total VOC

Figure 1 shows comparisons of measured and simulated 6-9 AM total VOC among the three sites that provided 1-hour VOC data: Sunol (SUNO, SFBA), Granite Bay (GNBY, SAC), and Parlier (PLR, SJV). Total VOC at Sunol is provided for July 31 and for the average over July 30 – August 1. It is interesting to note that on the day of highest ozone in the SFBA (July 31) the total VOC at Sunol is actually slightly lower than the 3-day average. Model performance is acceptable at Sunol and Granite Bay, but indicates a significant under prediction at Parlier by a factor of 2.5.

Figure 2 shows measured and simulated total VOC at 6-9 AM July 31 among the five SFBA 3-hour canister sites: Sunol (SUNO), Bodega Bay (BODB), San Leandro (LEAN), Bethel Island (BTI), and Patterson Pass (PATP). Insufficient data were available in the 3-hour dataset to construct 3-day averages or to show total VOC at Patterson Pass on July 31. All sites show under predictions, with model values at Bodega Bay and Bethel Island being low by about a factor of three. Note that canister data at Bodega Bay (a "background" site) indicate higher total VOC than Sunol. A comparison of 1-hour and 3-hour total VOC at Sunol on July 31 shows that the 3-hour VOC is higher by 35 ppbC, even though the 1-hour data contained significantly more hydrocarbon species than the 3-hour data (140 vs. 49). The reason for this is unclear.

Figure 3 presents total VOC at 6-9 AM August 1 at San Andreas (SGS, SAC) and Turlock (TSM, SJV), the only sites with sufficient 3-hour canister data in these regions. Both measurements are on par with 1-hour GC-MS data from Parlier. Both show under predictions, with San Andreas indicating that the model is low by more than a factor of 3.5.

Evaluation of CB-IV Speciated VOC

Figures 4 and 5 show the CB-IV species performance against 1-hour data at Sunol on July 31 and for the 3-day average, respectively. On July 31, the model performance is rather good and this agrees with performance for total VOC. For the 3-day average, performance for PAR is good but other species exhibit more of an under prediction bias by typically 50%.

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This is mainly due to higher measured values in the average while model values remain consistent with those on July 31. The missing contributions from FORM, ISOP, ETOH, and MEOH would generally contribute a few more ppbC to total VOC.

Figure 6 presents CB-IV species performance relative to 3-hour data at Sunol on July 31. This plot reveals the cause of the higher 3-hour measured total VOC at this site: PAR is nearly double the 1-hour value. Furthermore, TOL is more than doubled, and ALD2 shows a 5 ppbC contribution, both of which are severely under predicted.

Figures 7 through 10 display the CB-IV species at Bodega Bay, San Leandro, Bethel Island, and Patterson Pass. The severe under prediction of total VOC at Bodega Bay is due to PAR (93 ppbC measured vs. only 26 ppbC simulated), where the PAR prediction is primarily comprised of the 20 ppb boundary conditions. Model performance for other species is acceptable. If the PAR sample data are correct, then further investigation into its source is necessary (possibly fire activity well to the north) and this may need to be modeled through higher boundary and/or initial conditions. Similar performance is seen for San Leandro (Figure 8), where PAR is under predicted by ~30% and ALD2 is under predicted by a factor of 3. Performance for other species is acceptable. At Bethel Island (Figure 9), PAR is under predicted along with OLE and ALD2 (although not as severely as San Leandro). Bethel Island also exhibits a strange spike for MEOH. Much data are missing at Patterson Pass on July 31 (Figure 10), but for those CB-IV samples that are provided, model performance is generally acceptable. Note the much higher ALD2 in the data that is a consistent feature at most sites.

Moving to the Sacramento region, Figure 11 presents the model performance against 1-hour CB-IV measurements at Granite Bay on August 1. In this case, the slight over prediction of total VOC is caused by too much PAR; performance for other species appears to be acceptable. However, note the strange spike in ethanol (ETOH) in the measurement data. The only other site in this region with sufficient data to make a comparison is San Andreas. Figure 12 shows the 3-hour canister data for this site on August 1. Here there are under predictions in most species that exhibit concentrations of more than 1 ppbC, including PAR (the biggest contributor), OLE, FORM, and ALD2. Concentrations of TOL and XYL are appropriately low.

Finally, in the San Joaquin area, Figure 13 shows model performance against 1-hour CB-IV measurements at Parlier on August 1. The large under prediction of total VOC at this site (Figure 1) is seen to be caused by under predictions of CB-IV species virtually across the board, but especially for PAR and ALD2. Other reactive VOCs (OLE, TOL, XYL, ETH) are all low by factors of 3 to 6. Given that we consider the GC-MS data to be more robust than the canister dataset (based on consistently more samples and more chemical compounds per sample), this could be a significant finding. Note, however, that GC-MS data quality is highly dependent on field calibration and the general consensus among the chemists is that canister data is usually more reliable (when available) than the GC-MS data. At Turlock (Figure 14), model performance against the 3-hour canister data is much better and agrees rather well with most CB-IV species. While OLE is under predicted by a factor of 3, TOL and XYL are over predicted. The consistent under prediction of ALD2 appears at this site as well.

Analysis of VOC:NOx ratios

An analysis of VOC:NOx ratios was undertaken for those sites reporting both reliable VOC canister and GC-MS measurements and NOx data. Similarly to the analysis of VOCs reported above, the ratios were calculated for the 6-9 AM period for each day in which sufficient data were available. Results are shown in Table 1.

In the SFBA, 1- and 3-hourly observed and predicted VOC:NOx ratios were compared at Sunol, whereas 3-hourly ratios were compared at Bethel Island. Measurements from both sites show NOx-rich conditions and the predictions agree rather well with this. While VOC predictions agree with observations at Sunol, NOx is consistently under predicted. This is likely due to the close proximity of this site to freeway emissions that the grid model cannot resolve. The model varies between over and under predictions of both NOx and VOC at Bethel Island. The general agreement between observed and predicted VOC:NOx ratios in spite of generally poor performance for each component concentration in the SFBA suggests that emission are in basically correct proportion but that meteorological influences are playing a role in overall model performance (at least in the east bay).

In the Sacramento area, 1- and 3-hourly ratios were compared at Granite Bay (the only site with co-located instruments in the CCOS dataset). The data and model also both indicate NOx-rich conditions east of Sacramento, with model over predictions of both NOx and VOC on August 1. This may be due to an incorrect placement of the urban precursor plume on this day (a meteorological factor), but it does not suggest a significant problem with the proportion of emissions.

In the SJV, 1- and 3-hour ratios were calculated for Parlier and 3-hour ratios were determined for Turlock. At Parlier, the large under predictions of VOC (as described above) is causing a NOx-rich regime in the model while the measurement data inversely indicate a strong NOx-limited situation. NOx concentrations are also under predicted at Parlier, but not nearly to the extent of the VOC under predictions. At Turlock, the model is also far too NOx-rich, while the observed VOC:NOx ratio suggests conditions early in the episode that are much closer to optimum ozone formation potential. In this case, however, high VOC concentrations are replicated rather well on most days, and it is the over prediction of NOx that is driving the modeled VOC:NOx ratios downward. The simulated conditions in the SJV appear to be driven more by disproportionate emission estimates rather than meteorology.

Table 1. Compilation of observed and predicted 6-9 AM VOC and NOx concentrations at sites with co-located monitors in the CCOS air quality database. Data from both 1- and 3-hour instruments are shown for days in which data were available. Differences between observations and predictions greater than 30% are depicted in red.

Site / VOC sample duration / date		VOC (ppbC)	NOx (ppb)	VOC:NOx
Sunol 1-hr July 30	Obs	78	25	3.2
	Pred	65	16	4.1
Sunol 1-hr July 31	Obs	51	37	1.4
	Pred	55	23	2.4
Sunol 3-hr July 31	Obs	86	37	2.3
	Pred	59	23	2.6
Sunol 1-hr Aug 1	Obs	71	77	0.9
	Pred	62	27	2.3
Bethel Island 3-hr July 30	Obs	58	14	4.1
	Pred	109	20	5.6
Bethel Island 3-hr July 31	Obs	153	22	6.9
	Pred	64	17	3.7
Bethel Island 3-hr Aug 1	Obs	148	31	4.8
	Pred	63	13	4.9
Granite Bay 3-hr July 31	Obs	101	28	3.6
	Pred	106	27	4.0
Granite Bay 1-hr Aug 1	Obs	72	13	5.5
	Pred	97	28	3.4
Parlier 1-hr July 31	Obs	354	24	15.0
	Pred	83	15	5.7
Parlier 3-hr July 31	Obs	169	24	7.2
	Pred	92	15	6.3
Parlier 1-hr Aug 1	Obs	184	12	15.3
	Pred	76	13	5.8
Turlock 3-hr July 30	Obs	159	23	7.0
	Pred	139	44	3.1
Turlock 3-hr July 31	Obs	152	23	6.6
	Pred	132	54	2.4
Turlock 3-hr Aug 1	Obs	167	35	4.8
	Pred	126	43	2.9
Turlock 3-hr Aug 2	Obs	208	56	3.7
	Pred	140	57	2.5

Conclusions

Our conclusions from this analysis are as follows:

- The 3-hour canister data from most CCOS sites exhibited very few hydrocarbon species samples relative to the 1-hour GC-MS sites. Because of this, the 3-hour dataset did not provide sufficient information over CB-IV species and/or time period to allow inclusion into our analysis. We therefore believe the 1-hour data to be more robust. This finding invalidates our previous preliminary evaluation.

- In spite of the assertion above, there still exists large uncertainty concerning overall data quality in the CCOS VOC dataset, both for canister and GC-MS samples. While certain findings from the analysis reported here are significant, they may be overly influenced by the inclusion of poor quality samples that appear to be reasonable from casual inspection without further supporting evidence to suggest otherwise.

- We wish to stress that the performance results reported here should not be taken as an implication of the emissions inventory only. If we are to believe the measurement data, then certainly some aspects of the results (e.g., significant differences for certain species, disagreement among observed/predicted VOC:NOx ratios) are likely associated with deficiencies in emissions, either in total mass, speciation profiles, temporal profiles, spatial allocation, etc. However, there exists a large range of plausible explanations that involve meteorological performance (inaccurate mixing heights, wind field errors that cause the modeled urban plumes to miss the monitors, etc.), and at this point none of these should be ruled out.

- Generally, there are consistent model performance issues that we have identified in the three basins and among most sites with useable measurements. First, there is a general under prediction of total VOC and this is mainly attributable to insufficient PAR (since this contributes the bulk of VOC mass). Second, the model lacks sufficient levels of higher aldehydes (ALD2), usually by large factors of 2 or more. This is a surprising result and possible explanations are made difficult by the fact that model-to-sample comparisons are largely an "apples-oranges" dilemma. ALD2 in the model is primarily secondarily formed with some contributions from emissions (e.g, biogenics). ALD2 in the measurements is primarily from directly emitted hydrocarbon compounds, pieces of which are allocated to the CB-IV ALD2 bin for reactivity purposes (i.e., they are not necessarily carbonyl type compounds).

- VOC performance in the SFBA showed consistent under predictions of total VOC. A large discrepancy between 1-hour and 3-hour samples at Sunol (mainly PAR) remains unexplained. The Sunol site indicates under predictions for reactive species (OLE, TOL, XYL) in both 1-hour and 3-hour samples. There is evidence from Bodega Bay that background levels of PAR are too low, although this could be caused by old smoke plumes originating well to the north of the CCOS domain. Generally, performance for individual CB-IV species other than PAR was acceptable (with a few exceptions).

Limited VOC:NOx ratio data and predictions indicate that the east bay is NOx-rich.

- VOC performance in the Sacramento region indicates mixed performance for total VOC on August 1. Granite Bay indicates just a slight over prediction of 1-hour data, with generally good performance across CB-IV species, while San Andreas shows significant under predictions of 3-hour PAR, OLE, and carbonyls. There were insufficient data to compare 1-hour and 3-hour data at Granite Bay. Observations and predictions of VOC:NOx ratios at Granite Bay agree that conditions east of Sacramento are NOx-rich.

- VOC performance in the SJV region showed consistent under predictions of total VOC, with especially poor performance at the Parlier GC-MS site. CB-IV species were under predicted across the board at that site. Results in Turlock were better, with a slight under prediction of total VOC from low PAR, OLE, and ALD2. There were insufficient data to compare 1-hour and 3-hour data at Parlier. VOC:NOx analyses also suggest a problem with disproportional VOC and NOx emissions in the SJV.

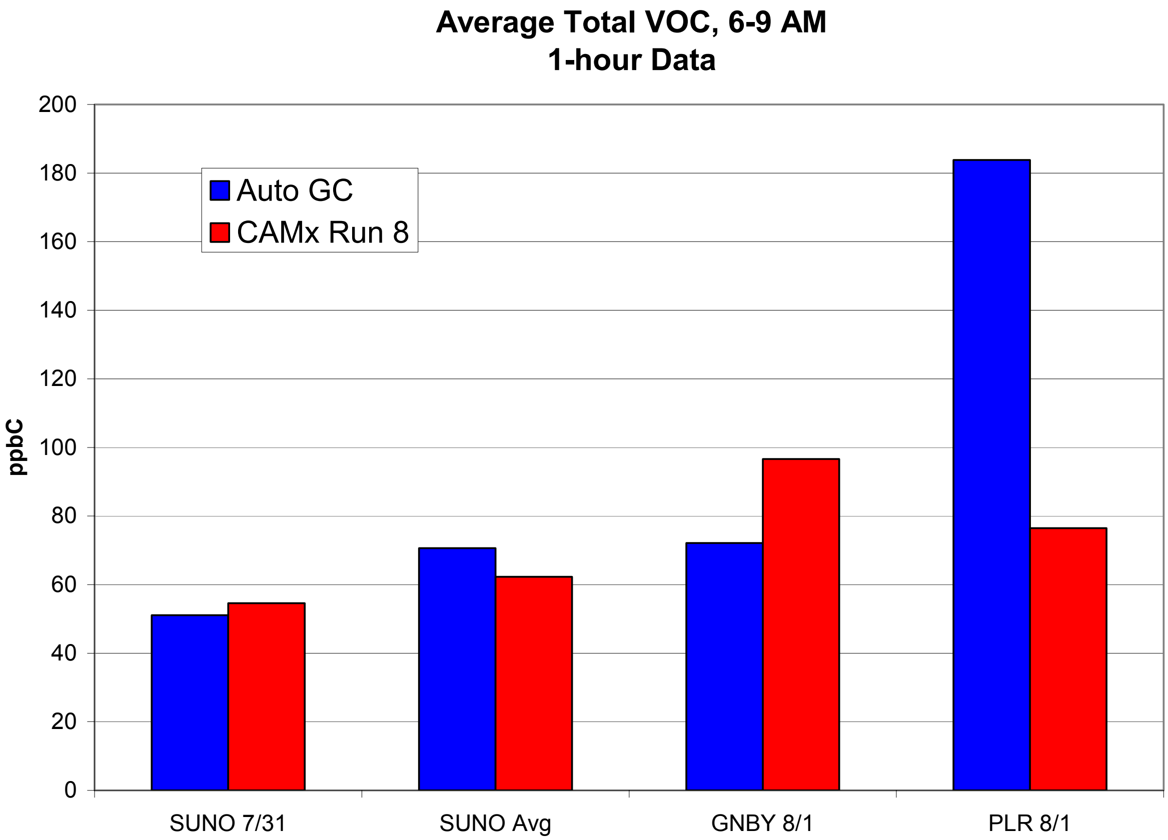

Figure 1. Total VOC measurements and predictions at three 1-hour GC-MS sites in the CCOS domain.

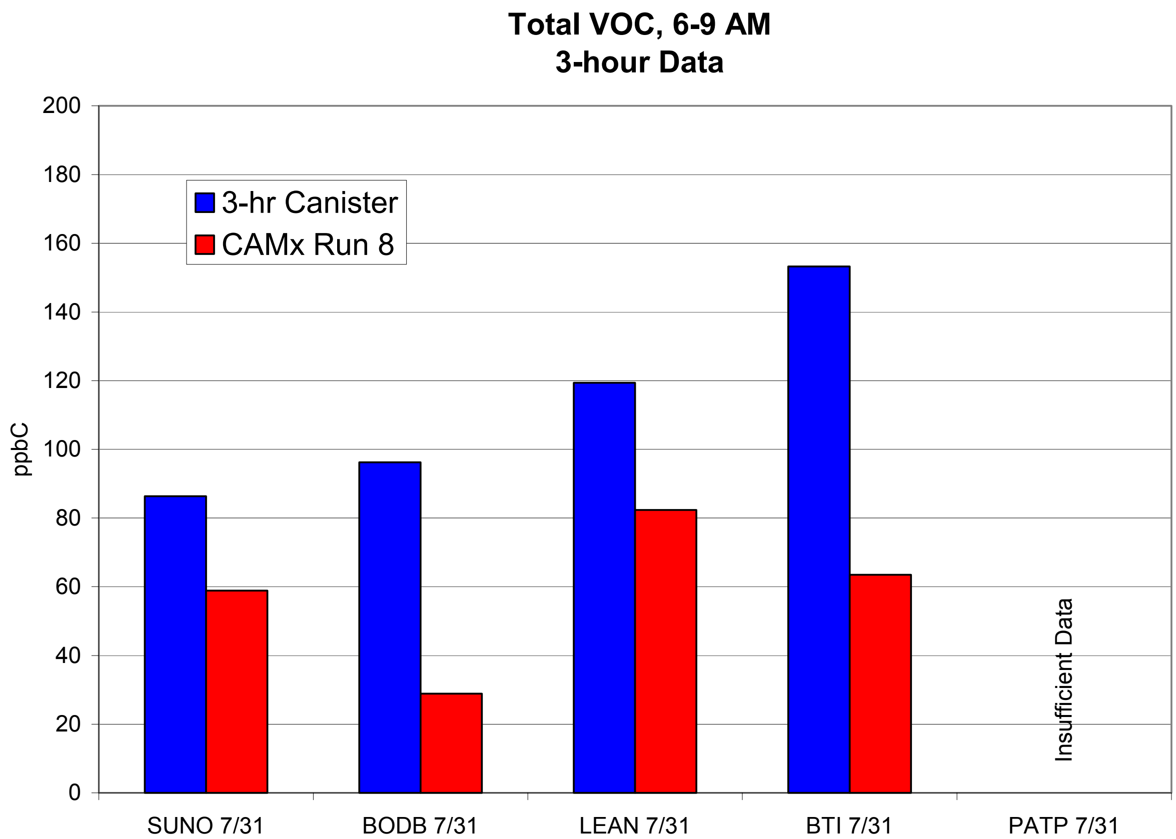

Figure 2. Total VOC measurements and predictions at five 3-hour canister sites in the SFBA region.

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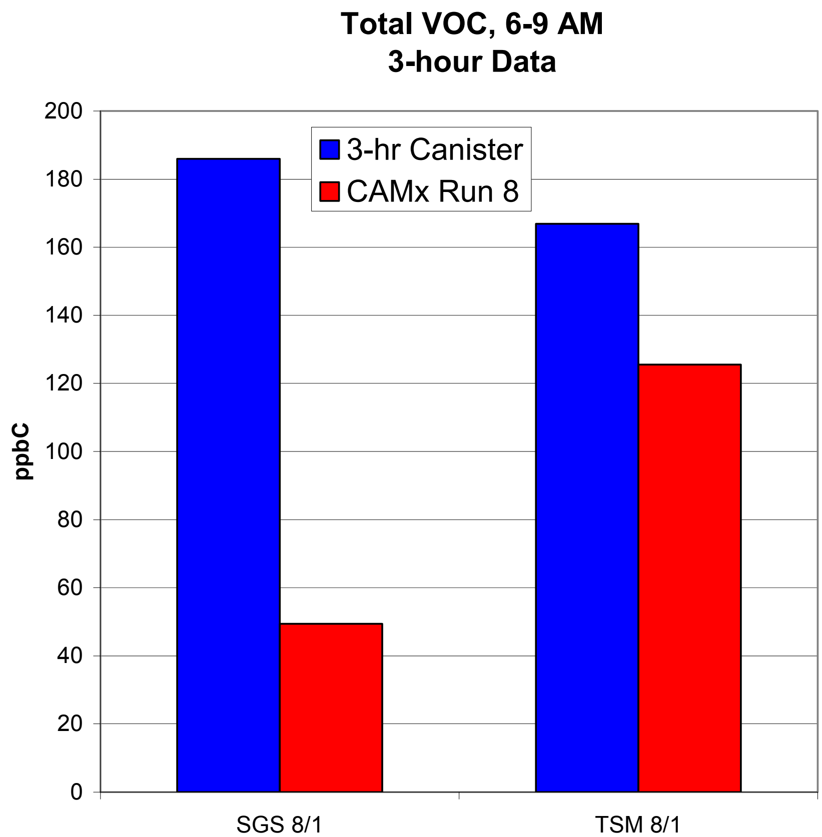

Figure 3. Total VOC measurements and predictions at two 3-hour canister sites in the SAC (SGS) and SJV (TSM) regions.

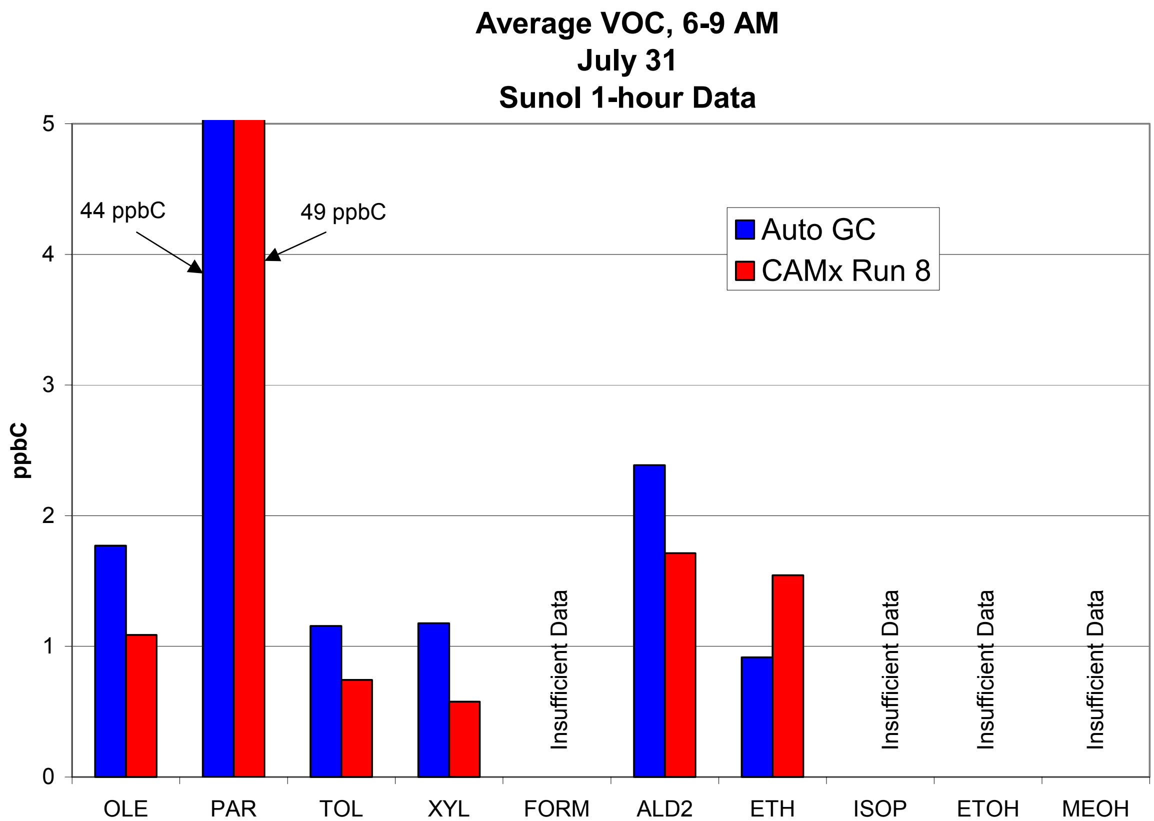

Figure 4. CB-IV speciated measurements and predictions at the Sunol 1-hour GC-MS site on July 31.

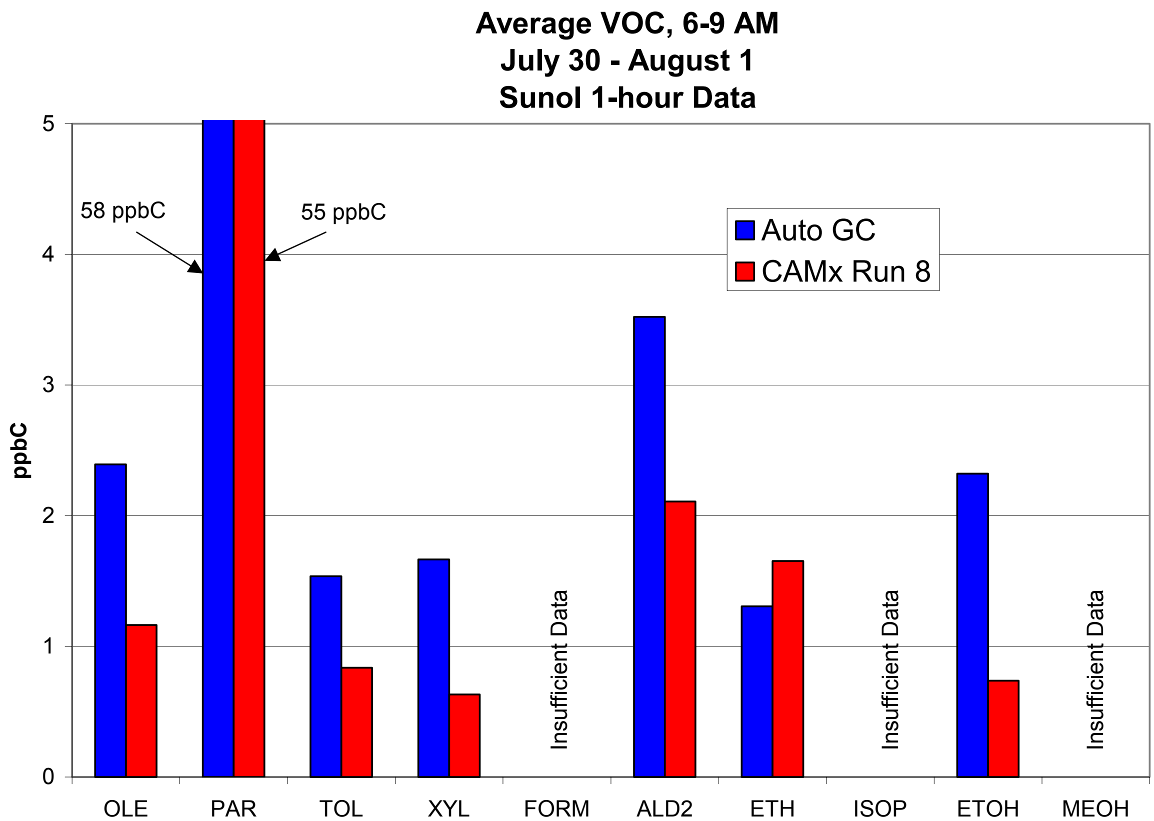

Figure 5. CB-IV speciated measurements and predictions at the Sunol 1-hour GC-MS site averaged over July 30 – August 1.

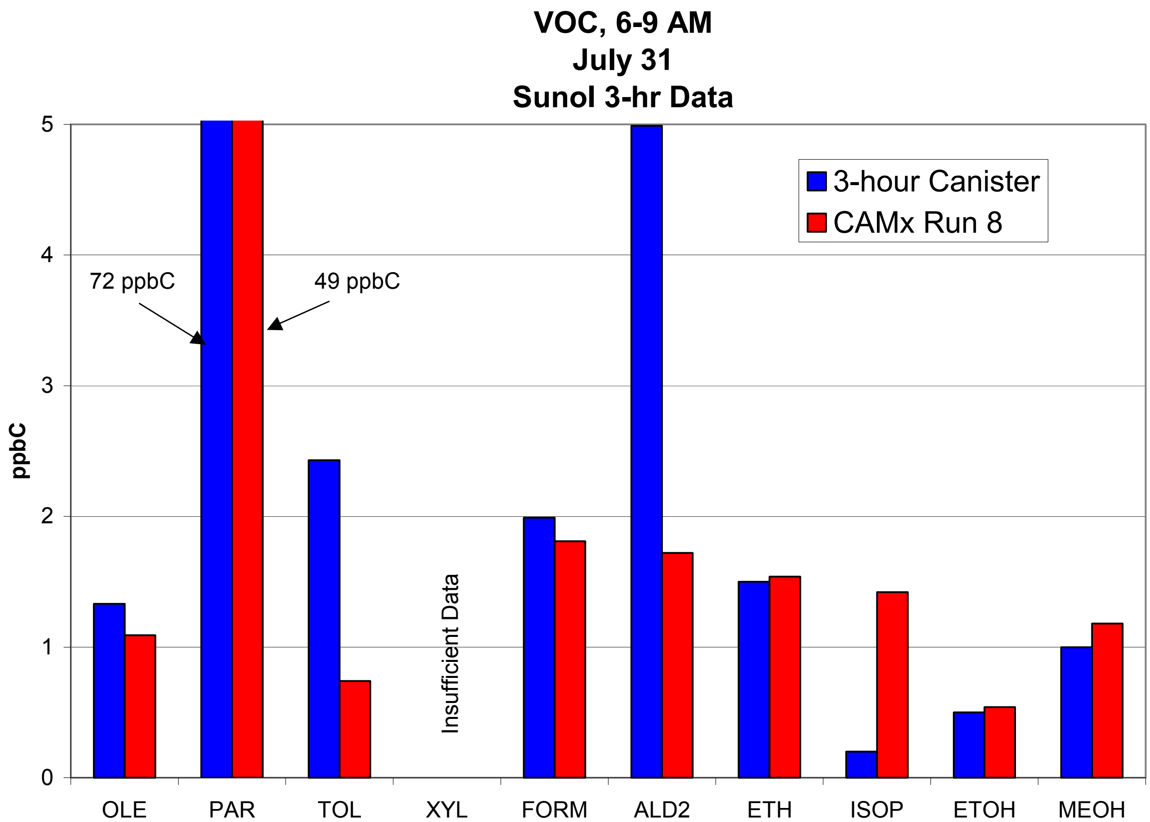

Figure 6. CB-IV speciated measurements and predictions at the Sunol 3-hour canister site on July 31.

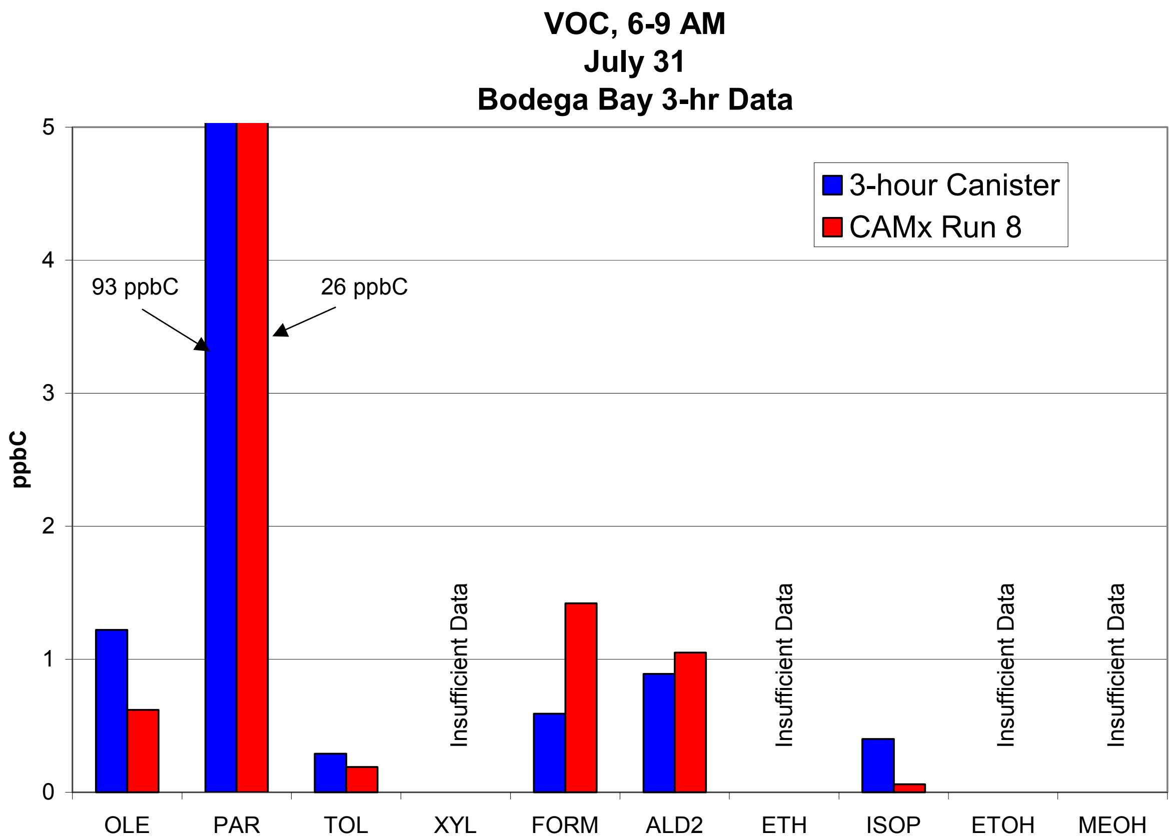

Figure 7. CB-IV speciated measurements and predictions at the Bodega Bay 3-hour canister site on July 31.

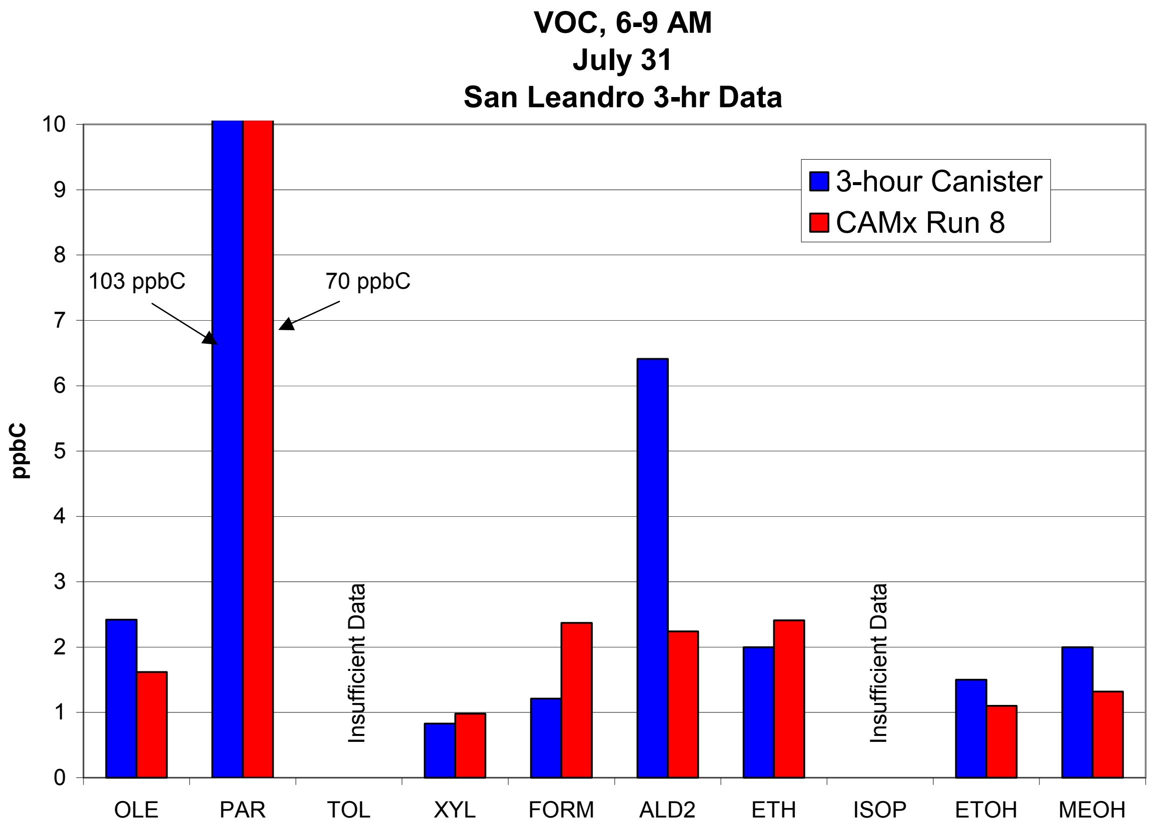

Figure 8. CB-IV speciated measurements and predictions at the San Leandro 3-hour canister site on July 31.

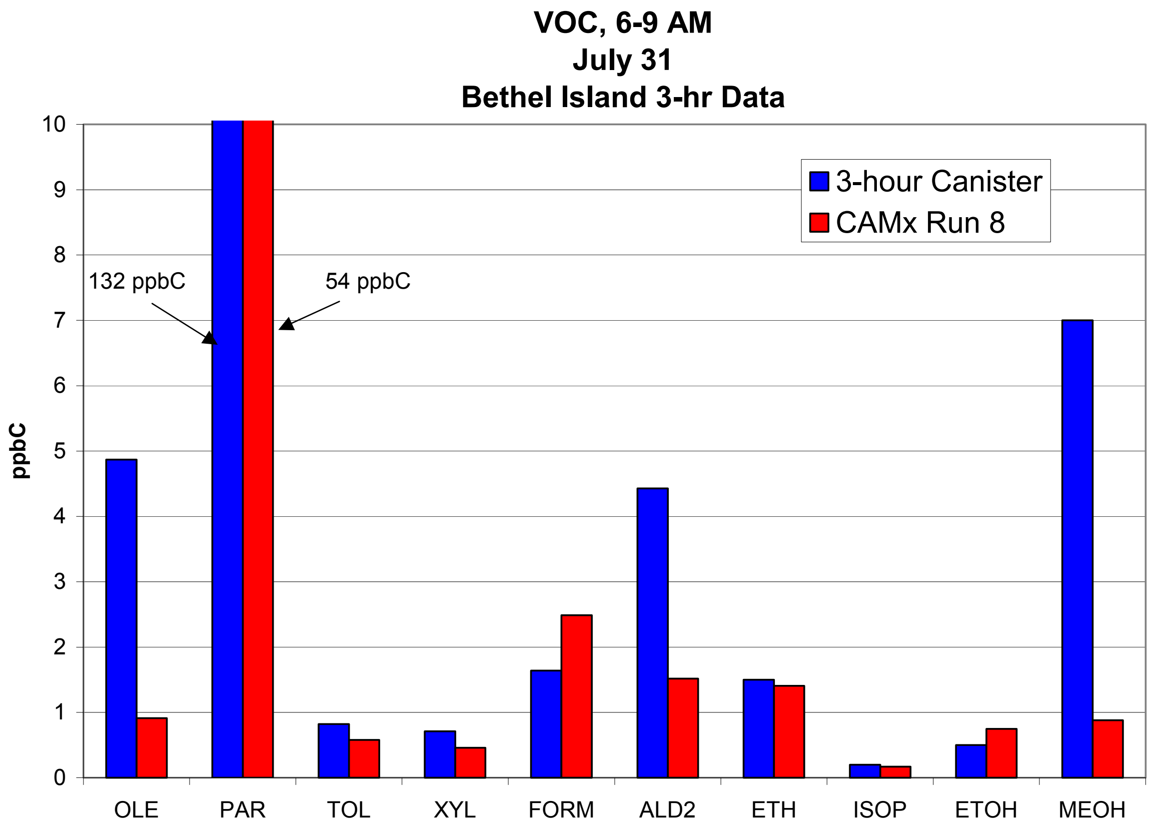

Figure 9. CB-IV speciated measurements and predictions at the Bethel Island 3-hour canister site on July 31.

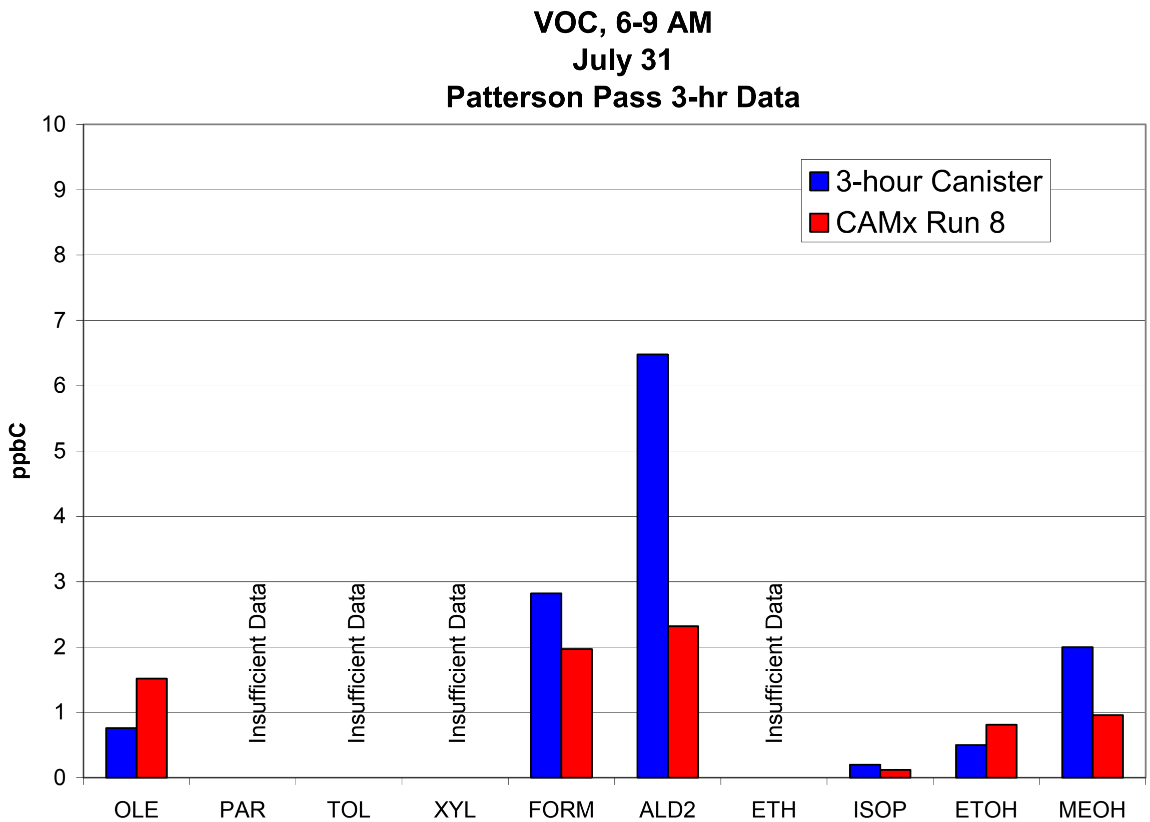

Figure 10. CB-IV speciated measurements and predictions at the Patterson Pass 3-hour canister site on July 31.

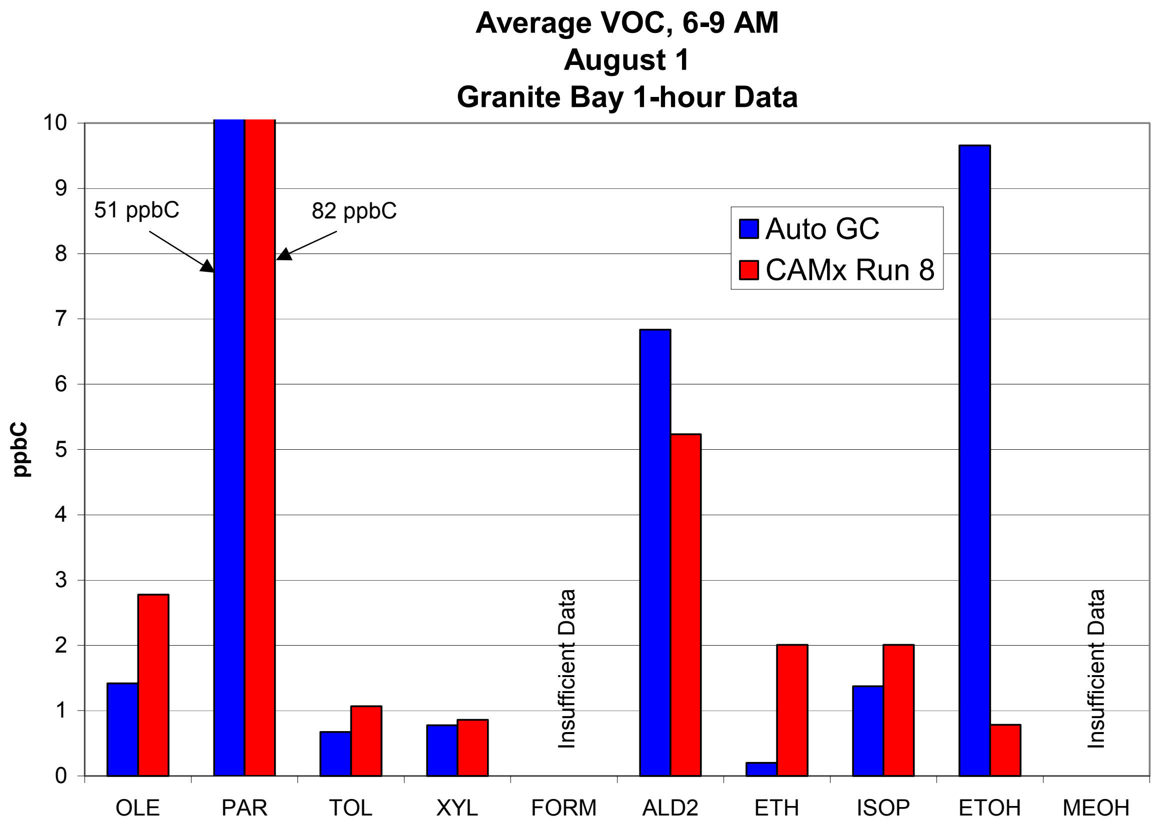

Figure 11. CB-IV speciated measurements and predictions at the Granite Bay 1-hour GC-MS site on August 1.

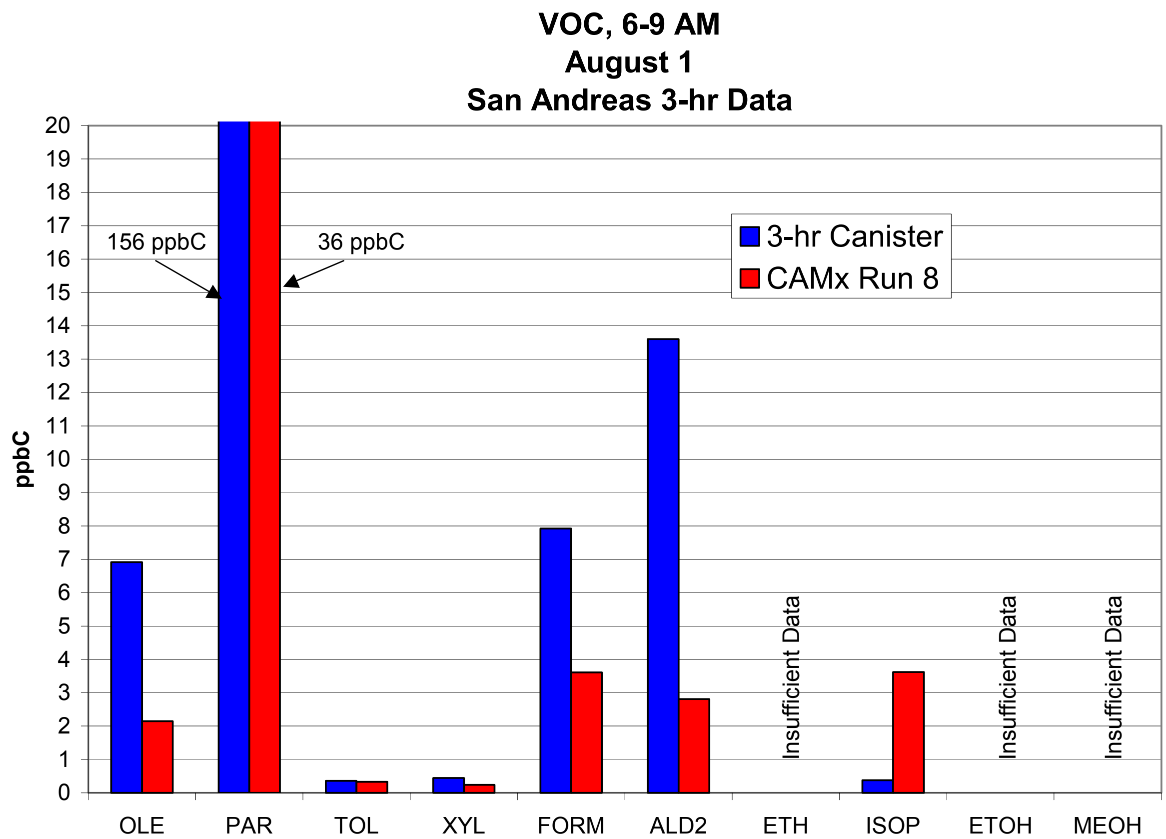

Figure 12. CB-IV speciated measurements and predictions at the San Andreas 3-hour canister site on August 1.

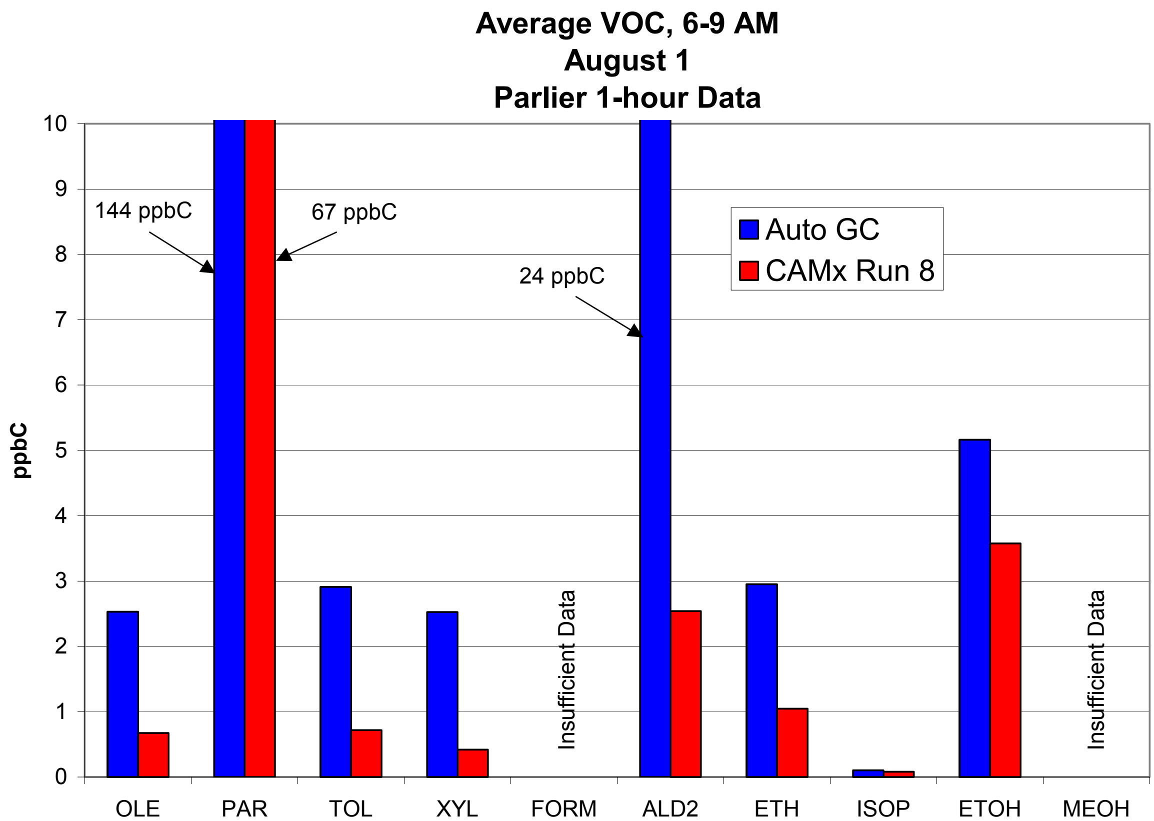

Figure 13. CB-IV speciated measurements and predictions at the Parlier 1-hour GC-MS site on August 1.

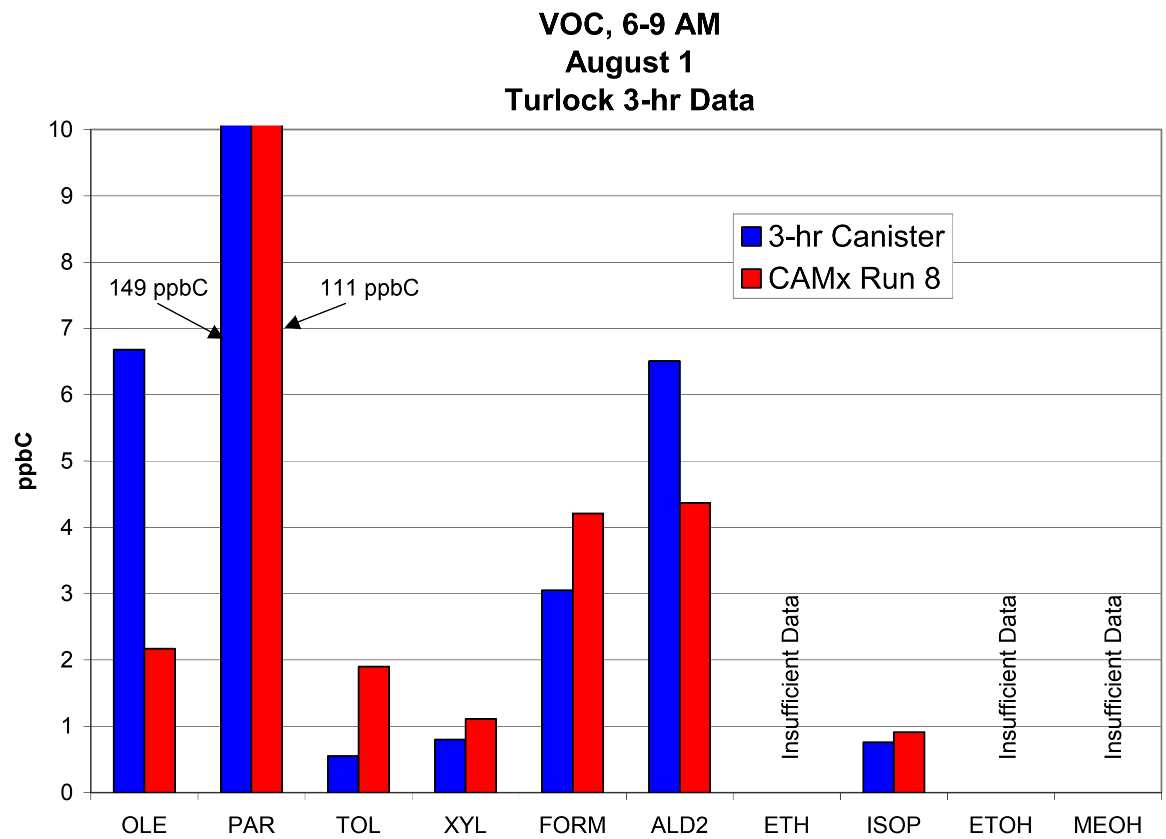

Figure 14. CB-IV speciated measurements and predictions at the Turlock 3-hour canister site on August 1.