

# **The Analysis of Ozone Precursors by AutoGC: The Role of Calibration and Quality Control Strategies in Data Management for Fully Automated Thermal Desorption-GC-FID Systems**

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**Carol J. Meyer**

Orsat LLC, 1416 E. Southmore Ave., Pasadena, Texas 77502

## **INTRODUCTION**

The analysis of ozone precursors has been a feature of the EPA air quality surveillance regulations since 1992 with the establishment of Photochemical Assessment Monitoring Stations (PAMS) as part of State Implementation Plans (SIP) for ozone non-attainment areas classified as serious, severe or extreme. At that time, guidance documentation allowed for the measurements of VOC precursors either by canister sampling or by continuous measurement using a GC-FID with a thermal desorber collecting hourly samples.<sup>1</sup> Only a few agencies chose to do continuous sampling and since that time a lot has been learned about the issues associated with the continuous field measurement of VOCs.

In 2011 the EPA initiated an effort to re-evaluate the PAMS requirements and the technology being used for continuous field measurements in conjunction with upcoming changes to the National Ambient Air Quality Standards (NAAQS) for ozone. With guidance from Clean Air Science Advisory Committee Air Monitoring Methods Subcommittee (CASAC AMMS) and National Association of Clean Air Agencies' (NACAA) Monitoring Steering Committee (MSC), the EPA promulgated revisions to the network design and is evaluating newer technology for continuous measurements. The new EPA ruling has recommended a redistribution of PAMS sites in an effort to increase the spatial coverage of this data for modeling performance evaluations.<sup>2</sup> More agencies may find themselves responsible for implementing continuous hourly volatile organic carbon (VOC) monitoring in conjunction with existing NCORE network sites. While this type of hourly AutoGC monitoring represents a significant increase in complexity in both implementation and data management, systems have been developed and deployed to fully automate and streamline data collection and management.

In conjunction with implementation of this type of monitoring, agencies must develop the necessary Quality Assurance Project Plan (QAPP) as well as the Standard Operating Procedures to accomplish this more enhanced monitoring. Simplification of the quality control strategies as well as calibration requirements will play a key role in the success of any monitoring plan. The identification and quantitation of up to 56 non-methane hydrocarbon (NMHC) species hourly requires a quality control strategy which is easy to implement and maintain. This work is designed to review current methods of calibration for such online systems and the results of

various methods on quality controls as well as ambient data. Two commercially available systems were employed in this study. The PerkinElmer Ozone Precursor system comprised of the Turbomatrix Thermal Desorber in conjunction with a Clarus Dual FID Gas Chromatograph equipped with a Dean's switch has been used extensively in operations in Texas for over 20 years.<sup>3</sup> This system has been completely automated using the Totalchrom Data System in conjunction with automation software supplied by Orsat, LLC. Additionally, an Agilent GC-FID system equipped with a Dean's switch and coupled with the Markes Unity Thermal Desorption system was automated using Agilent CDS EZChrom software for unattended operation.<sup>4</sup>

## **THE CALIBRATION OF TD-GC-FID AUTOGC SYSTEMS**

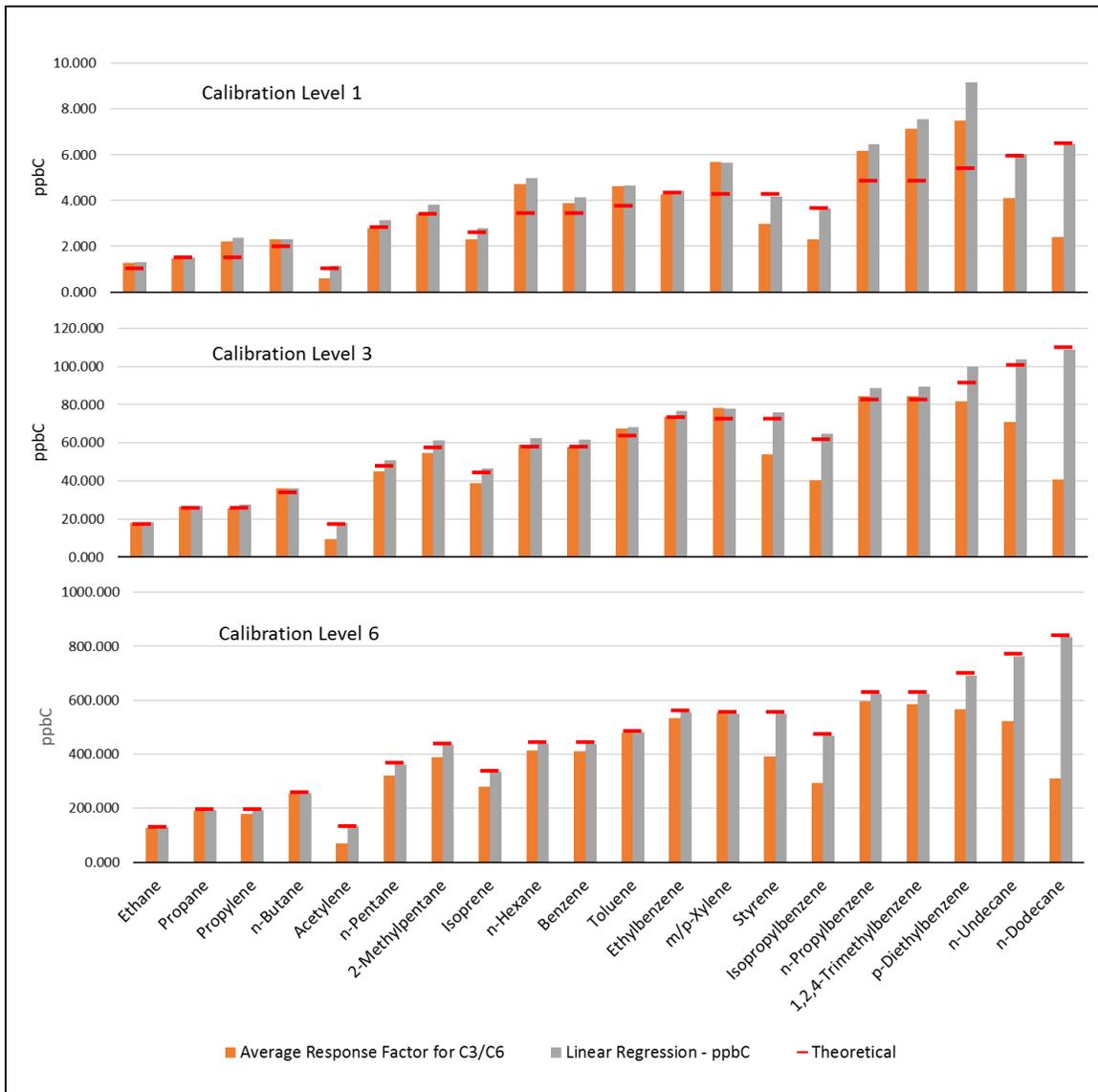
Current historical PAMS VOC data represents data which has been collected either by continuous on-line sampling or by collections of discrete samples in passivated SUMMA<sup>®</sup> canisters which are later analyzed in the laboratory environment. Most, if not all, on-line systems currently contributing data to the Aerometric Information Retrieval System (AIRS) Database maintained by the EPA are 40 minute samples of ambient air collected hourly and analyzed by GC-FID while those samples collected and returned to the laboratory are often analyzed using the same or similar methods to those used for air toxics using GC-FID, GC-MS or a combination of these methods. In both cases samples are concentrated in the same fashion by collection onto a cryogenically cooled multi-adsorbent trap and then thermally desorbed into the analytical system. A number of inter-laboratory comparisons have been done in an attempt to ascertain the comparability of data across large networks.<sup>5,6,7</sup>

These comparisons have shown that a majority of the NMHC data collected using TD-GC-FID is calibrated using carbon based calibration strategies. This calibration strategy is recommended in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (TAD) published by the EPA in 1998.<sup>1</sup> This type of calibration utilizes the response to propane to calibrate to a carbon based response factor which is applied to each target resulting in quantitation in ppbC rather than a molar calibration. On-line systems utilizing dual columns and dual FIDs utilize the benzene response to generate and apply a separate carbon response factor to the second channel to accommodate potential variations due to any slightly different response of the second detector/column system. While a calibration curve is still used to prove linearity across the analyzed range, a single response factor based on the average response across the range is used. This simplifies the review and error checking which is necessary to insure all targets are being quantified correctly. Although new data systems allow for automatic generation of linear or polynomial curves to generate unique response curves for each analyte, problems can arise if these calibration curves are not reviewed. The review and quality assurance which may be necessary to maintain a method which encompasses 56 analytes would be time consuming compared with the simple review of a maximum of two response factors applied universally for all targets. Even so there is the possibility of bias in the simpler calibration strategy.

To this end, calibrations were generated using both strategies and applied to the same data set for a commercially available on-line system comprised of an Agilent gas chromatograph and the Markes International Unity 2 Thermal desorption system to show the ultimate results of each calibration method on the data set. Calibration standards used were generated from a 56 component PAMS standard with a starting concentration of 100 ppbv using a dynamic dilution

system manufactured by Merlin MicroScience (MMSD-VOC) capable of generating gas mixtures from 0.5 ppbv to 70 ppbv. Using the chromatographic data system, methods were generated with multipoint linear calibration curves forced through zero for each analyte and alternatively using averaged carbon response factors generated based on propane for one channel and benzene for the other. Once calibrated methods were generated, the same calibration data were then run as unknowns and the reported concentrations compared to the theoretical concentration derived from the blend ratio and the certified concentration in the diluted standard. Figure 1 illustrates the concentrations reported by both methods relative to the theoretical of a selected number of target species on three of the six levels used for the calibration curve. There are some biases recognized to occur based on typical operational issues.

**Figure 1. Reported Concentration vs. Theoretical Concentration for Different Calibration Methods**



Typically, analytes which may have even a small contribution in the system blank show higher than predicted values on the lowest level such as propylene, m/p-xylene, n-propylbenzene and 1,2,4- trimethylbenzene. Small contributions from the system have a greater effect on the lowest calibration level (1) and show little effect on the highest level. This effect is irrespective of either method of calibration. The carbon-based calibration shows a low bias for a number of targets. Targets of higher boiling point show lower than predicted results due to irreversible adsorption within the system both by steel surfaces and the trapping material itself. This bias is normalized by using the component specific linear regression calibration. Table 1 represents the relative percent difference of the reported concentrations compared to the theoretical values for both calibration methods at the lowest dilution. Although there is some significant and predictable bias in the high boiling targets the average deviation from theoretical for all targets is actually higher for the linear regression method across all targets.

**Table 1. The Relative Percent Different between the Theoretical and Reported Concentrations at 0.5 ppbV**

PLOT Target	Linear Regression	Average RF Propane	BP Target	Linear Regression	Average RF Benzene
	RPD	RPD		RPD	RPD
Ethane	-25.0%	-23.7%	n-Hexane	<b>-37.4%</b>	<b>-31.8%</b>
Ethylene	-20.1%	-17.1%	Methylcyclopentane	-6.4%	2.7%
Propane	0.0%	2.4%	2,4-Dimethylpentane	-7.1%	2.9%
Propylene	<b>-45.2%</b>	<b>-37.2%</b>	Benzene	-19.4%	-12.8%
Isobutane	-13.0%	-5.7%	Cyclohexane	-8.5%	2.5%
n-Butane	-14.1%	-14.2%	2-Methylhexane	-15.9%	-13.5%
Acetylene	-12.3%	<b>50.2%</b>	2,3-Dimethylpentane	-9.7%	-1.1%
trans-2-Butene	-12.7%	-9.1%	3-Methylhexane	-7.1%	1.5%
1-Butene	-12.1%	-7.4%	2,2,4-Trimethylpentane	-5.3%	-3.7%
cis-2-Butene	-10.3%	-7.9%	n-Heptane	-8.0%	-3.4%
Cyclopentane	-9.0%	2.6%	Methylcyclohexane	-15.0%	-11.5%
Isopentane	-9.8%	8.4%	2,3,4-Trimethylpentane	-9.0%	-4.6%
n-Pentane	-11.2%	1.0%	Toluene	-21.3%	-20.7%
trans-2-Pentene	-9.1%	7.8%	2-Methylheptane	-9.6%	-9.9%
1-Pentene	-8.5%	11.2%	3-Methylheptane	-7.9%	-7.6%
cis-2-Pentene	-8.1%	9.9%	n-Octane	-8.1%	-5.1%
2,2-Dimethylbutane	-9.7%	6.4%	Ethylbenzene	-2.7%	1.4%
2,3-Dimethylbutane	-9.6%	6.1%	m/p-Xylene	-27.6%	-28.1%
2-Methylpentane	-12.2%	-0.8%	Styrene	2.5%	<b>35.9%</b>
3-Methylpentane	-9.7%	6.6%	o-Xylene	1.2%	2.2%
Isoprene	-6.5%	11.7%	n-Nonane	-9.1%	-3.6%
1-Hexene	-9.5%	9.3%	Isopropylbenzene	-0.3%	<b>45.5%</b>
<b>Average</b>	<b>-12.6%</b>	<b>0.5%</b>	n-Propylbenzene	-28.2%	-23.8%
			m-ethyltoluene	-2.5%	6.1%

PLOT Target	Linear Regression	Average RF Propane	BP Target	Linear Regression	Average RF Benzene
	RPD	RPD		RPD	RPD
			p-Ethyltoluene	-0.1%	11.8%
			1,3,5-Trimethylbenzene	3.0%	14.6%
			o-Ethyltoluene	-0.9%	-7.4%
			1,2,4-Trimethylbenzene	<b>-43.5%</b>	<b>-37.8%</b>
			n-Decane	-6.1%	8.5%
			1,2,3-Trimethylbenzene	7.5%	27.7%
			m-Diethylbenzene	4.8%	20.9%
			p-Diethylbenzene	<b>-51.6%</b>	<b>-32.5%</b>
			n-Undecane	-1.1%	<b>36.5%</b>
			n-Dodecane	0.6%	<b>91.9%</b>
			<b>Average</b>	<b>-10.3%</b>	<b>1.6%</b>

## THE EFFECTS OF CALIBRATION METHOD ON DATA

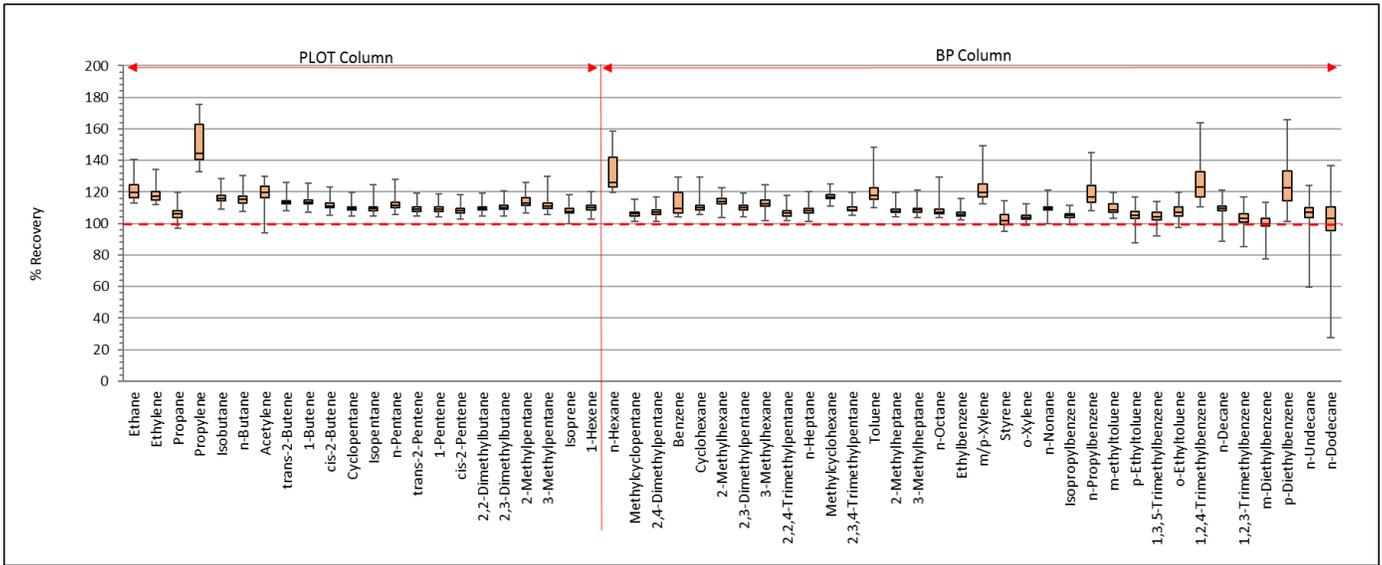
Ambient data from within the laboratory was collected over a period of three and a half months in addition to daily check standards at 0.5 ppbv and blanks. A second source laboratory check standard and retention time standard was also run as well as collection of data for the estimation of method detection limits (MDL) based on 40 CFR, Part 136, Appendix B.<sup>8</sup> All data was processed with each method and the results compared for both quality control checks as well as the ambient data set.

### Daily Check Standards

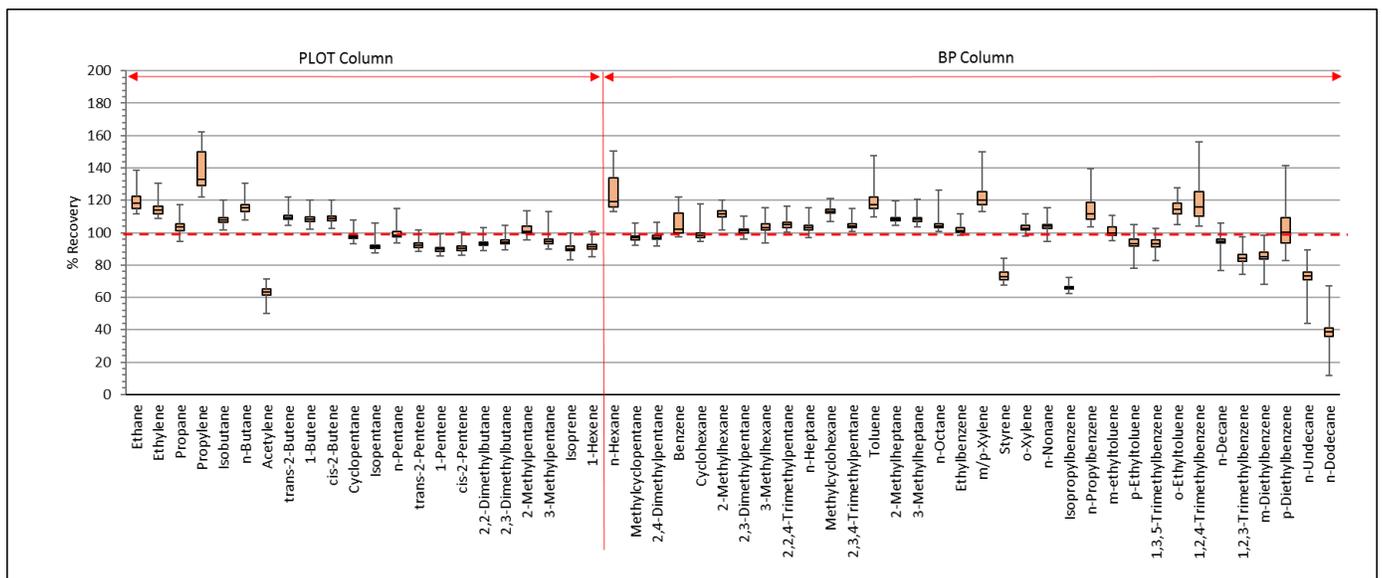
The system was configured to automatically introduce a daily check standard which was generated by dynamic dilution of a 100 ppbv PAMS standard containing the 56 target compounds to be analyzed. An additional collection was made daily of the diluent gas used in the dilution system to serve as the system blank. Zero air used both for the FID flame gases and the dilution system was generated by a compressor and purified using a Parker Zero Air purifier. Merlin EZSequence© software was used to generate sequences for the EZChrom data system capable of producing unique filenames which allowed easy identification of the quality control data. A calibration curve was generated using the dynamic dilution system comprised of 6 levels ranging from 0.5 ppbv to 70 ppbv. This data was used to generate both the target specific linear regression method and an average carbon response factor based on propane and benzene which was used across all targets based on their respective columns. After the 3.5 months of data was collected it was later reprocessed using both methods for comparisons shown here. Data was validated and data removed where system failures were evident however no attempt to specifically censor the data for outliers was made. The goal of this study was to determine the differences specifically of the method of calibration and any excursions in the data would be inherent in both data sets.

Figures 2 and 3 are box plot representations of the range of percent recoveries calculated from the daily check standard for the linear regression method and the average response factor method respectively. Check standard data spans a period of 3.5 months and includes 170 measurements. As discussed earlier, there is evident bias shown by the lower recoveries on some targets when a carbon-based response factor is used. However, in addition there are several noteworthy issues. The large uncertainty shown in the recoveries for propylene and hexane appear to transcend the calibration method. These variations can be attributed to common operational issues seen in this field analysis. Propylene is commonly found in ambient samples particularly in industrial areas. In addition, it is a common contaminant of analytical systems. Even at relatively low levels this

**Figure 2. Check standard percent recovery based on linear regression calibration method**



**Figure 3. Check standard percent recovery based on average carbon response method using propane and benzene**



analyte can concentrate in the Nafion® drier used for the removal of moisture from the ambient sample and this generally necessitates cleaning and/or replacement of the drier periodically. Hexane likewise can be affected by instrumental variables. The analysis requires the light gases to be eluted from the boiling point column into the PLOT column for separation. This instrument utilizes a Dean's switch to re-direct the effluent of the boiling point column to the second detector after the elution of 1-hexene. This switch can result in an excursion or even to cut into the eluting hexane peak causing variable integrations of this target resulting in the higher uncertainty in the measurements.

In general, however the results show losses of higher boiling analytes as well as acetylene and styrene which produces the commonly seen bias in the carbon-based response on these field systems.

### Minimum Detection Limit

To further evaluate the comparability of the two calibration methods samples were generated from the dilution system at the 0.5 ppbv level and used to calculate the minimum detection limit (MDL) as outlined in the TAD according to Appendix B to Part 136 of 40 CFR. Table 2 represents the MDL results for data analyzed with each method. The relative percent difference is calculated and differences greater than 30% are highlighted. Note that the significant differences exist as expected for those targets shown in the original calibration tests to have a less than expected carbon response in the analysis.

**Table 2. Minimum Detection Limit based on 40 CFR Part 136 Appendix B**

Target	Linear Regression				Average C3/C6 Response				MDL RPD
	n	SD	MDL	Ambient Min	n	SD	MDL	Ambient Min	
Ethane	7	0.039	0.102	0.909	7	0.038	0.101	0.909	1.3%
Ethylene	7	0.023	0.062	0.214	7	0.023	0.060	0.214	3.1%
Propane	7	0.046	0.122	1.822	7	0.045	0.119	1.822	2.4%
Propylene	7	0.046	0.121	0.463	7	0.042	0.112	0.463	8.3%
Isobutane	7	0.025	0.067	0.353	7	0.024	0.062	0.353	7.4%
n-Butane	7	0.014	0.037	1.193	7	0.014	0.037	1.193	-0.1%
Acetylene	7	0.017	0.045	0.035	7	0.009	0.024	0.035	61.5%
trans-2-Butene	7	0.012	0.031	0.058	7	0.011	0.030	0.058	3.6%
1-Butene	7	0.011	0.029	0.024	7	0.011	0.028	0.024	4.8%
cis-2-Butene	7	0.012	0.031	0.022	7	0.012	0.031	0.022	2.4%
Cyclopentane	7	0.016	0.043	0.035	7	0.014	0.038	0.035	11.6%
Isopentane	7	0.015	0.040	1.268	7	0.013	0.034	1.268	18.2%
n-Pentane	7	0.016	0.043	0.035	7	0.014	0.038	0.035	12.1%
1,3-Butadiene	7	0.008	0.021	0.014	7	0.008	0.020	0.014	2.4%
trans-2-Pentene	7	0.011	0.029	0.081	7	0.009	0.025	0.081	16.9%
1-Pentene	7	0.023	0.061	0.080	7	0.019	0.050	0.080	19.6%
cis-2-Pentene	7	0.008	0.020	0.112	7	0.006	0.017	0.112	18.0%
2,2-Dimethylbutane	7	0.021	0.056	0.051	7	0.018	0.047	0.051	16.1%

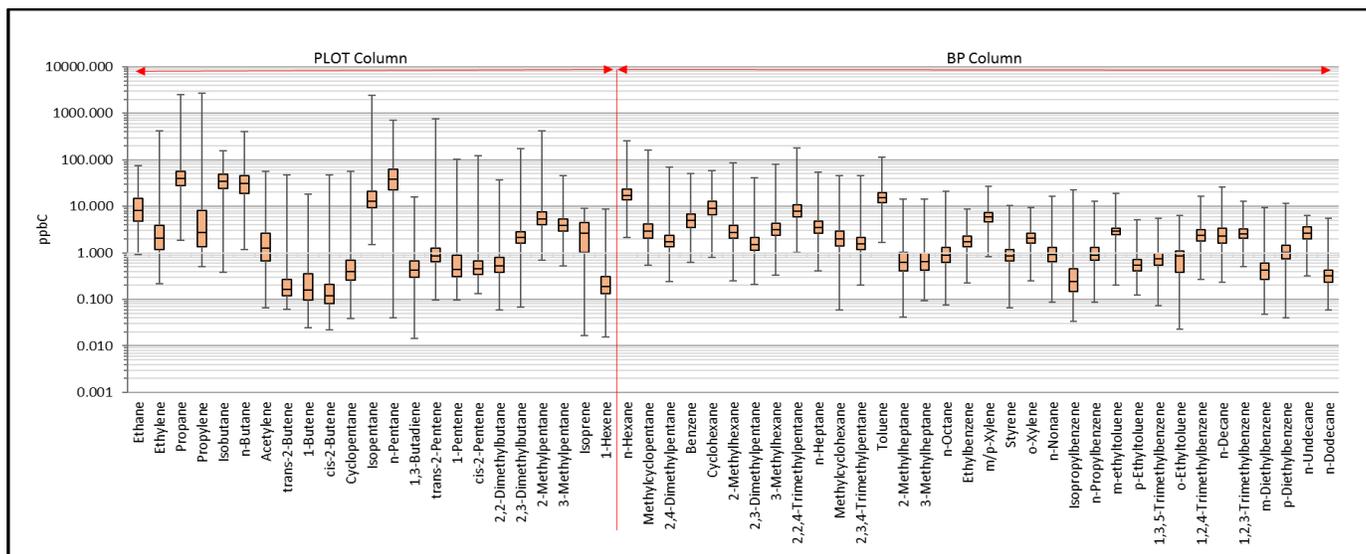
Target	Linear Regression				Average C3/C6 Response				MDL RPD
	n	SD	MDL	Ambient Min	n	SD	MDL	Ambient Min	
2,3-Dimethylbutane	7	0.018	0.046	0.057	7	0.015	0.040	0.057	15.7%
2-Methylpentane	7	0.022	0.059	0.622	7	0.020	0.053	0.622	11.3%
3-Methylpentane	7	0.023	0.062	0.451	7	0.020	0.053	0.451	16.2%
Isoprene	7	0.020	0.053	0.014	7	0.017	0.044	0.014	18.2%
1-Hexene	7	0.028	0.074	0.013	7	0.023	0.061	0.013	18.8%
n-Hexane	7	0.260	0.688	2.000	7	0.245	0.650	2.000	5.7%
Methylcyclopentane	7	0.018	0.048	0.500	7	0.017	0.044	0.500	9.8%
2,4-Dimethylpentane	7	0.027	0.072	0.218	7	0.025	0.066	0.218	9.3%
Benzene	7	0.030	0.080	0.592	7	0.028	0.075	0.592	6.2%
Cyclohexane	7	0.034	0.090	0.714	7	0.031	0.081	0.714	10.2%
2-Methylhexane	7	0.132	0.350	0.240	7	0.129	0.342	0.240	2.6%
2,3-Dimethylpentane	7	0.060	0.160	0.192	7	0.055	0.146	0.192	9.0%
3-Methylhexane	7	0.111	0.295	0.306	7	0.102	0.271	0.306	8.4%
2,2,4-Trimethylpentane	7	0.024	0.064	1.014	7	0.024	0.062	1.014	2.3%
n-Heptane	7	0.024	0.064	0.386	7	0.023	0.061	0.386	4.8%
Methylcyclohexane	7	0.041	0.108	0.057	7	0.040	0.105	0.057	3.5%
2,3,4-Trimethylpentane	7	0.025	0.067	0.197	7	0.024	0.065	0.197	3.5%
Toluene	7	0.026	0.069	1.682	7	0.026	0.068	1.682	1.6%
2-Methylheptane	7	0.023	0.062	0.042	7	0.023	0.062	0.042	0.0%
3-Methylheptane	7	0.023	0.062	0.091	7	0.023	0.062	0.091	0.0%
n-Octane	7	0.032	0.084	0.073	7	0.031	0.082	0.073	2.4%
Ethylbenzene	7	0.021	0.057	0.216	7	0.020	0.054	0.216	5.1%
m/p-Xylene	7	0.030	0.079	0.844	7	0.030	0.080	0.844	-0.3%
Styrene	7	0.065	0.173	0.047	7	0.046	0.123	0.047	34.2%
o-Xylene	7	0.084	0.223	0.248	7	0.083	0.220	0.248	1.3%
n-Nonane	7	0.029	0.077	0.083	7	0.028	0.074	0.083	4.7%
Isopropylbenzene	7	0.052	0.138	0.021	7	0.033	0.087	0.021	45.5%
n-Propylbenzene	7	0.039	0.102	0.084	7	0.037	0.098	0.084	3.9%
m-ethyltoluene	7	0.094	0.250	0.186	7	0.086	0.229	0.186	8.5%
p-Ethyltoluene	7	0.058	0.155	0.109	7	0.052	0.138	0.109	11.6%
1,3,5-Trimethylbenzene	7	0.123	0.326	0.065	7	0.110	0.290	0.065	11.6%
o-Ethyltoluene	7	0.123	0.326	0.024	7	0.131	0.348	0.024	-6.6%
1,2,4-Trimethylbenzene	7	0.060	0.159	0.253	7	0.057	0.150	0.253	6.1%
n-Decane	7	0.048	0.127	0.201	7	0.041	0.109	0.201	15.3%
1,2,3-Trimethylbenzene	7	0.061	0.162	0.418	7	0.050	0.132	0.418	20.3%
m-Diethylbenzene	7	0.073	0.194	0.041	7	0.062	0.165	0.041	16.3%
p-Diethylbenzene	7	0.091	0.240	0.033	7	0.074	0.196	0.033	20.3%
n-Undecane	7	0.096	0.254	0.217	7	0.066	0.174	0.217	37.4%
n-Dodecane	7	0.329	0.872	0.115	7	0.123	0.325	0.115	91.3%
Average			0.132				0.111		

## Ambient Data

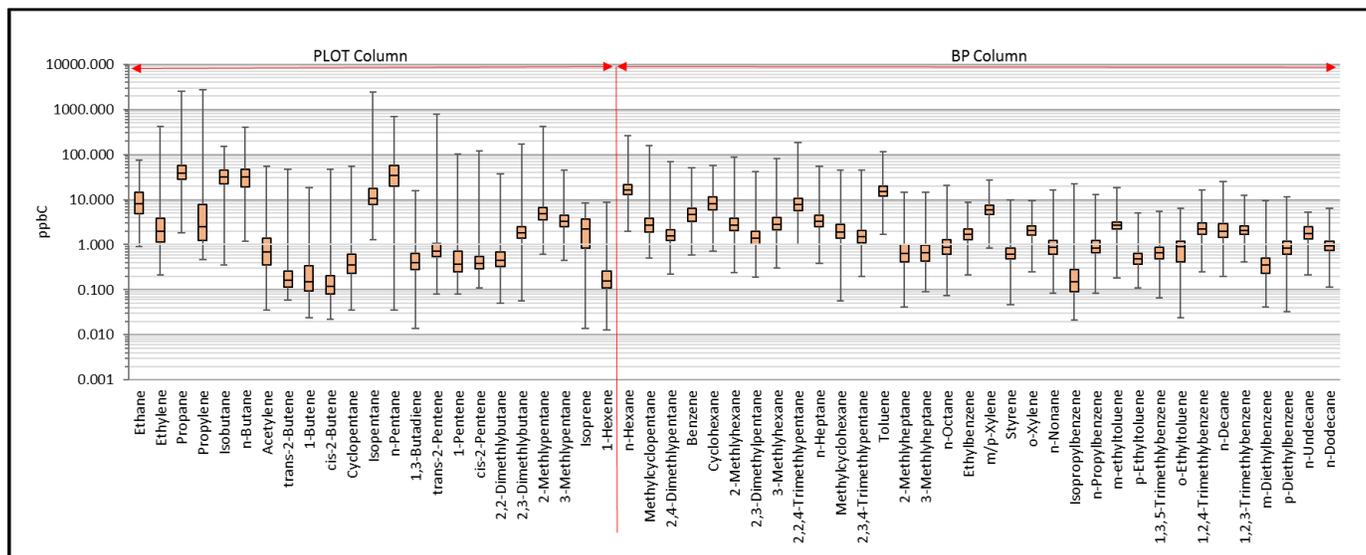
To determine the degree that this affects the monitoring data the two calibration methods were applied to both ambient measurements to determine if the method of calibration substantially impacts these measurements.

Figures 4 and 5 represent the same box plots of over 1900 ambient measurements over the 3.5-month period processed with the linear regression and carbon based response factor methods.

**Figure 4. Distribution of ambient concentrations for 1974 measurements using linear regression calibration**



**Figure 5. Distribution of ambient concentrations for 1974 measurements using an average carbon response method using propane and benzene**



Again, data was only censored for obvious equipment malfunction and no attempt was made to remove possible outliers.

What is most evident is the lack of significant differences in the ambient data as a population between the two calibration strategies. Neither acetylene or styrene show significant differences in the ambient data regardless of calibration method and even though checks show losses of heavier hydrocarbons which the linear calibration should address, this is not evident in ambient data. This may partly be related to the fact that a large percentage of ambient measurements fall below 1 ppbC and uncertainty in the measurement is higher. Table 3 reports the relative distribution of measurements above and below 1 ppbC for both analytical data sets.

**Table 3. Distribution of ambient concentrations over 3 ½ months**

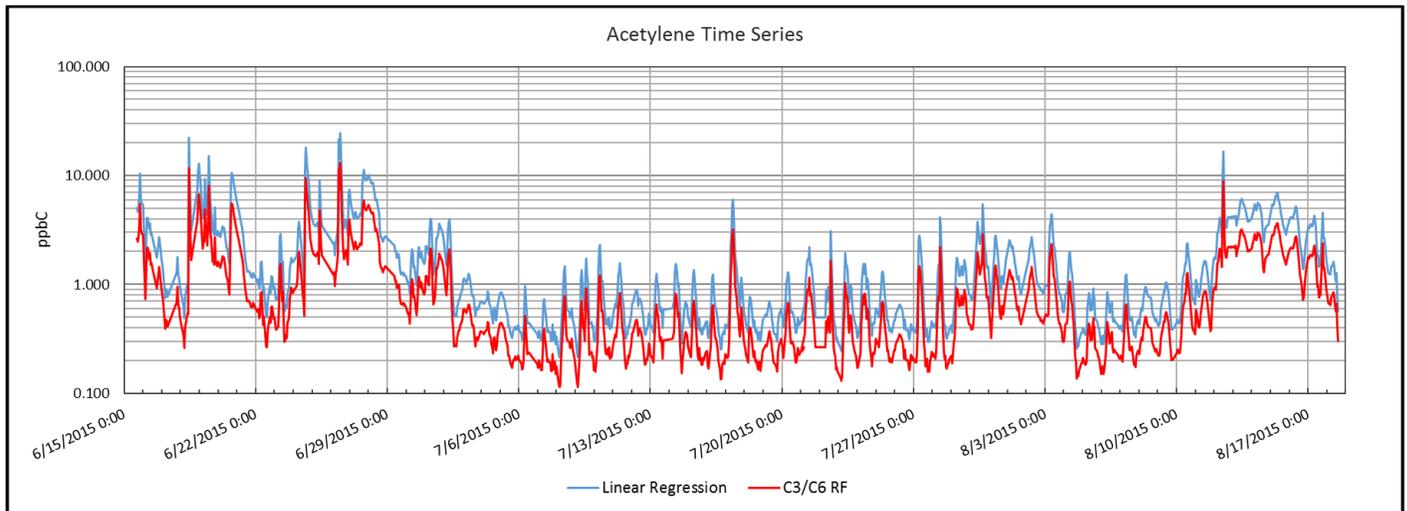
Linear Regression			Average C3/C6 Response Factor		
Concentration ppbC	Number of Measurements	%	Concentration ppbC	Number of Measurements	%
ND	253	0.2%	ND	248	0.2%
<1.0	38,636	34.4%	<1.0	40,776	36.3%
>10	16,501	14.7%	>10	15,615	13.9%
>100	532	0.5%	>100	435	0.4%
<b>Total Measurements</b>	112,208			112,213	

However, another factor is the potential bias related to the check standards and indeed even the calibration standards are a source of bias which may not exist in ambient data. It should be noted that the evaluation of check standard samples may represent a bias in the ability to generate, sample and measure the check standard itself and may not be representative of ambient measurements. The difficulties in approximating humidity and uniformity in quality control and calibration standards may well result in sampling bias which does not exist in the sampling of ambient air.

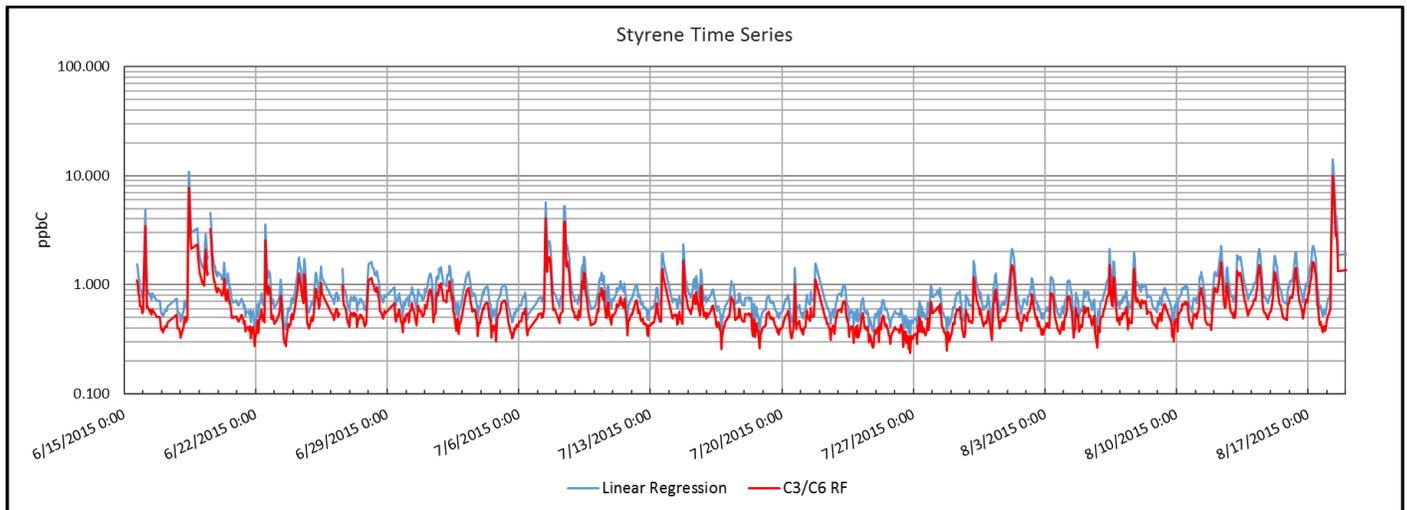
A final comparison was made on the ambient data in an attempt to see the effects of the calibration on the data. A common method used to review ambient data for modeling purposes involves the use of both time series and scatter plots to evaluate special and temporal differences such as diurnal patterns as well as relationships between species which may facilitate source determination. In light of this, the time series plots for acetylene and styrene were compared since these two species demonstrated large discrepancies between calibration methods.

Figures 6 and 7 depict the comparative time series for acetylene and styrene respectively. As can be observed the time series for each only varies slightly in concentration, thus while the accuracy of the measurement may be different, the precision appears to be good and is not affected by the method of calibration. Since these measurements are in the range of 1-3 ppbC it is difficult to determine which method is truly more accurate.

**Figure 6. Comparative time series of concentrations in ppbC for acetylene calculated with a linear regression calibration vs. a carbon response factor calibration**



**Figure 7. Comparative time series of concentrations in ppbC for styrene calculated with a linear regression calibration vs. a carbon response factor calibration**

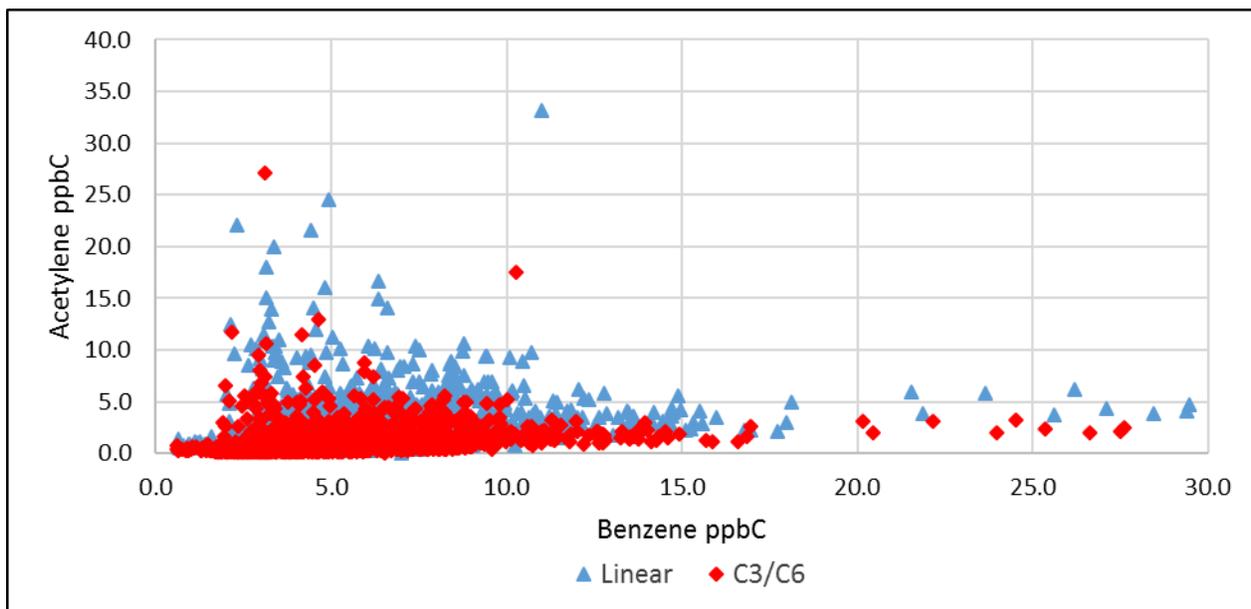


Likewise, the comparative scatter plots in Figures 8 and 9 represent the relationships between acetylene and benzene as well as for styrene and ethylbenzene. These also show only a slight shift in the response based on the calibration differences. Again, this suggests that the effect seen in the actual artificially derived standards may not be inherent in the ambient air measurements. Overall, the effect of calibration method on these ambient measurements may affect the absolute values but do not appear to change the trends as seen in the ambient population of data.

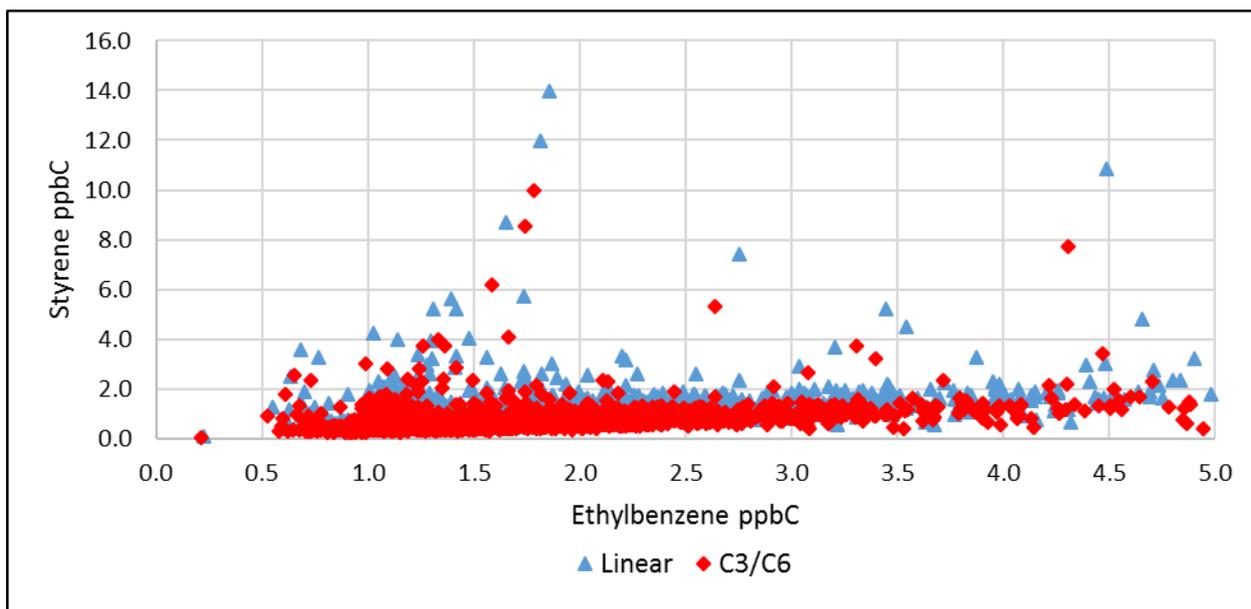
## SUMMARY

While there is a definite difference in the results on tested samples manufactured either in canisters or by dynamic dilution it is important to remember that the linear regression method of calibration does not remove the lower responses seen across targets. Since the carbon response

**Figure 8. Scatter plot of relationship between acetylene and benzene**



**Figure 9. Scatter plot of relationship between styrene and ethylbenzene**



of the FID has been thoroughly studied and characterized the bias across hydrocarbon species is more likely a function of the thermal desorption process itself and the hardware associated with it. Moreover, this bias may result from the attempt to manufacture suitable test mixtures and may not represent a systematic error in the corresponding ambient measurements.

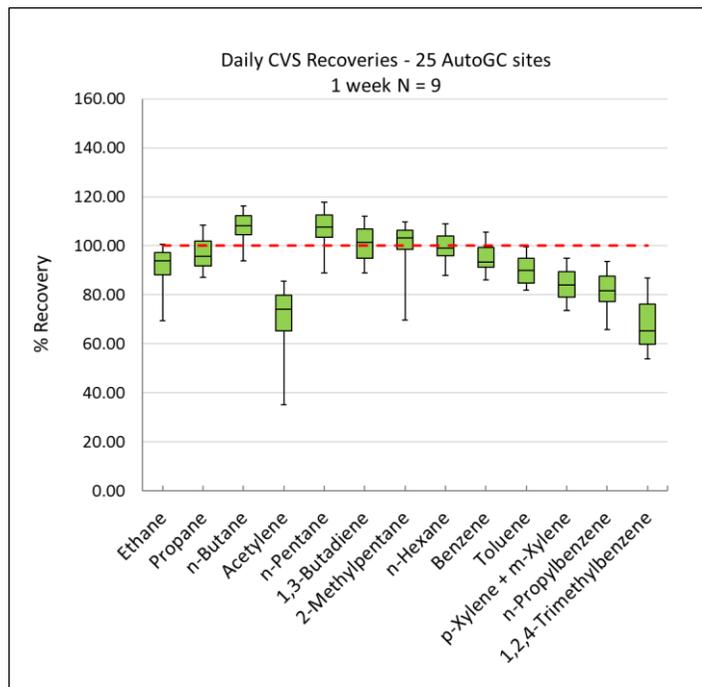
The implementation of currently available continuous, online AutoGC systems like the ones used here involves more than just a fully automated system. Care must be taken to design a quality management system which is simple and robust to minimize both operator scrutiny and

maximize both data quality and data completeness. Systems must be not only well calibrated but designed to make any calibration errors readily observable to validation team members. Although there are observable differences in the calibration methods used for this analysis, consideration must be given to the complexity of the calibration process as well as the ease with which errors can be observed in such a calibration. Existing NMHC data being used in modeling efforts is based on the carbon-based response strategy and thus consideration must be given to historical data despite biases which may be inherent in this data.

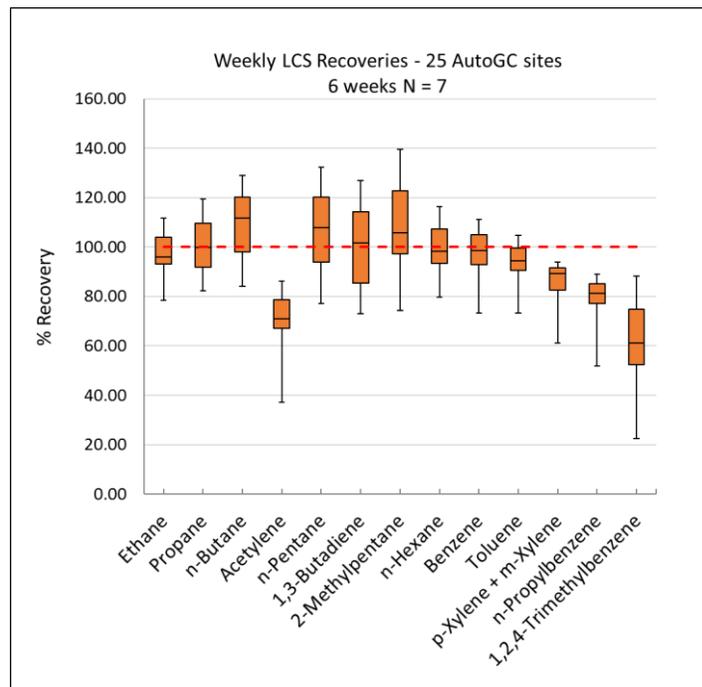
To build a population of data for use in modeling it is important that all data be generated in a similar fashion. While the differences shown here between calibration methods may appear to be of little consequence on the actual data collected, the method of calibration could affect both the overall quality of the data and data recovery. Compound specific linear regression calibration is difficult at best when performed by highly trained laboratory personnel. The use of this type of calibration strategy may result in errors which ultimately would result in faulty measurements and lost data. The ease with which a carbon-based average response factor calibration strategy can be implemented facilitates more frequent calibration without the intense scrutiny required of target specific calibration curves.

Carbon-based calibration has been in use in the PAMS program since its inception in 1993. Using the PerkinElmer Ozone Precursor systems, the Texas Commission on Environmental Quality (TCEQ) has been operating AutoGCs for over 20 years and currently has 37 field systems collecting hourly data year round. With a robust network and sound quality control program, the TCEQ is able to see consistent results from many systems. Figure 10 illustrates the combined daily calibration verification standard (CVS) recoveries for 15 targets across 25

**Figure 10. Distribution of daily CVS recoveries for 25 sites over 1 week**



**Figure 11. Distribution of weekly LCS recoveries for 25 sites over 6 weeks**



PerkinElmer AutoGC systems during a week (9 measurements per system). The CVS is a 1 ppmv 15 component certified standard which is diluted to 5 ppbv. The inherent bias is shown for the heavier hydrocarbons and acetylene but this bias is reproduced throughout the network uniformly and consistently. Figure 11 shows a second source laboratory check standard (LCS) which is run weekly at each site as well. This standard is blended statically from another 1 ppmv certified standard to 5 ppbv in a canister and run to validate the dynamic dilution system. Figure 11 represents weekly measurements at 25 sites over a 6-week period or 7 measurements per site. While the variation is slightly larger, the network consistency is evident and the bias still observable.

By implementing good repeatable instrument configurations as well as monitoring instrument performance via frequent quality control checks, these systems are able to generate large amounts of consistent data across the range of targets.

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