Value-added Hardware Application

Support for

- Markes-Agilent PAMS AutoGC systems
- PerkinElmer Ozone Precursor Systems

Including

All additional hardware for field operation including

- Hydrogen Generator with auto-restart and power failure backup
- TOC Generator for low dew-point, hydrocarbon-free air supply
- Zero air purifier for hydrocarbon-free FID air
- Oil-less compressor
- All heated, silco-treated sample lines

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Orsat is a third-party service organization specializing in the automation and support services for PAMS AutoGC Systems. Offer services and support for PE and Agilent Systems. With over 20 years of experience in operating AutoGC systems for PAMS Ozone precursor analysis in Texas, Louisiana and Georgia, Orsat currently supports and operates over 30 continuous analyzers in Texas. We have experience in every aspect of operation and validation of AutoGC data.

Value-added Hardware Application

- Purpose
  - Provide installation and configuration of Ozone Precursor system for field deployment
  - Supply the necessary hardware modifications for automation of quality control samples
  - Provide software to generate sampling sequences which include quality control samples and file naming structure which identifies files by sample types, date and time and site designation
  - Provide dilution system for generation of check standards and calibration curves from 1 ppm
- Results
  - Systems will be field ready and field tested.

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Purpose of our Value-added Hardware Application is to provide the elements specific to a turn-key continuous monitoring solution using these Lab-scale GC systems. We can configure, supply hardware and automation for continuous operation including routine quality control samples. We provide software to generate sequences which control the introduction of routine QC samples as well as generation of calibration curves. Our solution will result in a field ready – field tested solution.

Value-added Hardware Application

- What you will get
  - MMSD-VOC-MPV Dilution system
  - EZVOC Software
    - EZSequence for generating 24 day sequences
    - Mmove for archiving and moving files for polling
  - Configuration of all necessary valves and relays for automating introduction of quality control samples along with heated sample lines
  - Configuration of all necessary instrument and processing methods
  - All the plumbing, fittings, regulators and additional purifiers necessary to make a fully field ready system including necessary support gas systems.
- What we can do for you:
  - Deployment to your field location
  - Field Qualification for 1 week to meet specifications
  - Train operators and validators

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What you get:
1. A dilution system to generate calibration curves from a 1 ppmC calibration gas
2. Software to generate sequences which will interface with our additional valving installed and configured to introduce routine QC samples
3. Configuration of all necessary analytical methods
4. Complete configuration of all plumbing and support gas systems

What we can do:
1. Deployment
2. Field Qualification for 1 week to meet specification
3. Training for operators and validators

Also available:
Support contracts

Automation for Introduction of Quality Control Samples

- Automatic introduction of QC samples
  - Dynamically diluted check standard
  - Analytical blank
- Automatic dilution of multipoint calibration curve
- Dilution from 1 ppm multi-component standard to 1 ppb
- Low diluent gas consumption
- No mass flow controllers

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Each system will have automatic introduction of quality control samples and is designed for uninterrupted data collection. Each system is equipped with its own dynamic calibration system capable of automatically introducing daily calibration checks and analytical blanks as well as multipoint calibration points.

Data Handling

- EZChrom OpenLab CDS Workstation
  - Files easily portable off-site for review and reprocessing if necessary
  - Single data file which contains all method information
  - Ability to generate method from datafile to reproduce data analysis parameters
  - Generation of ASCII format output or cross-tab output
  - Offline instrument to allow review of data on site computer
- Second EZChrom CDS Workstation at remote location
  - Review data without risk of interruption or arbitration of data collection
  - Reprocess data where necessary

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OpenLab EZChrom was chosen because it generates data files which are easily transported to another computer where they can be reviewed and reprocessed if necessary. It also can generate ASCII text output for ingestion into other systems. We recommend the purchase of a second copy of the data system to be used offline at a remote location to reduce the risk of interfering with on-going monitoring activities to facilitate the review and reprocessing of any data.

OpenLab EZChrom CDS

- Peak Identification
  - Retention time windows
  - Peak RT References to adjust for drift
  - Slope and Skim settings to refine peak integration
- Calibration by average carbon response factor can be entered manually
- Noise threshold to reduce interference from overly sensitive peak detection
- Width sensitivity settings to minimize detection of spurious non-chromatographic peaks.

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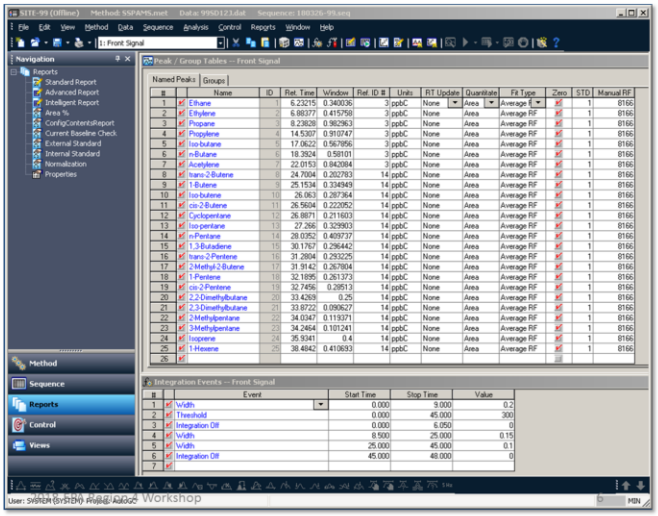
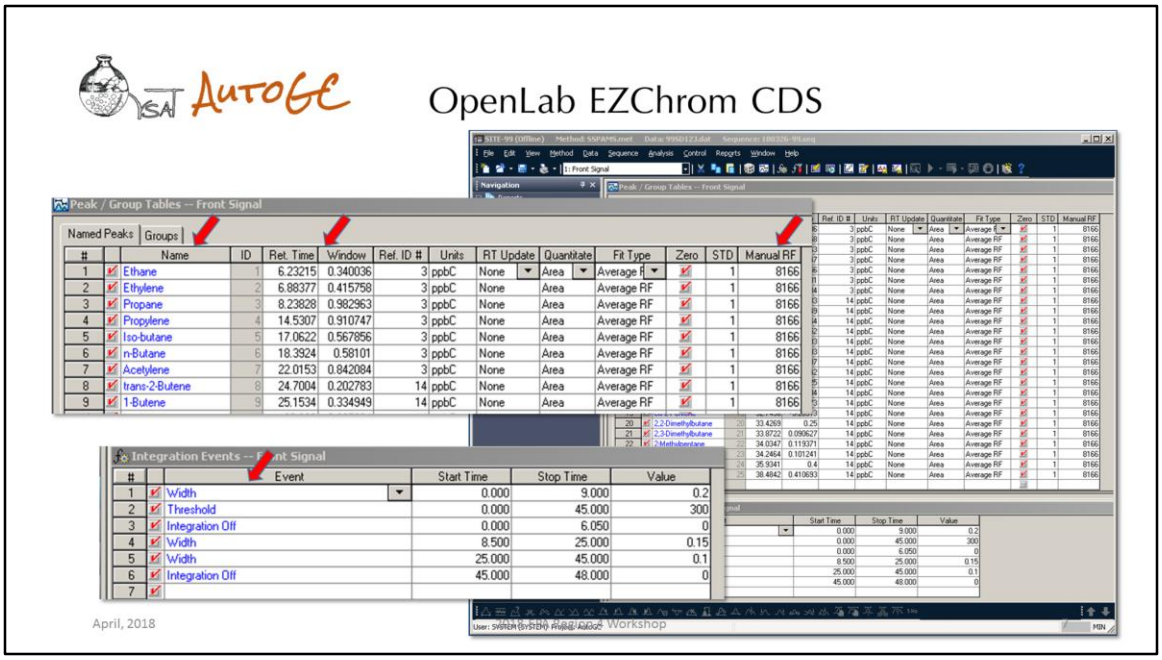


The EZChrom Data System

1. Identifies components using retention time windows and uses reference peaks to accommodate routine diurnal drift
2. Quantitates components using an average response factor based on Propane and Benzene
3. Allows for noise thresholds to reduce interference
4. Uses a width sensitivity setting to minimize detection of spurious non-chromatographic peaks.



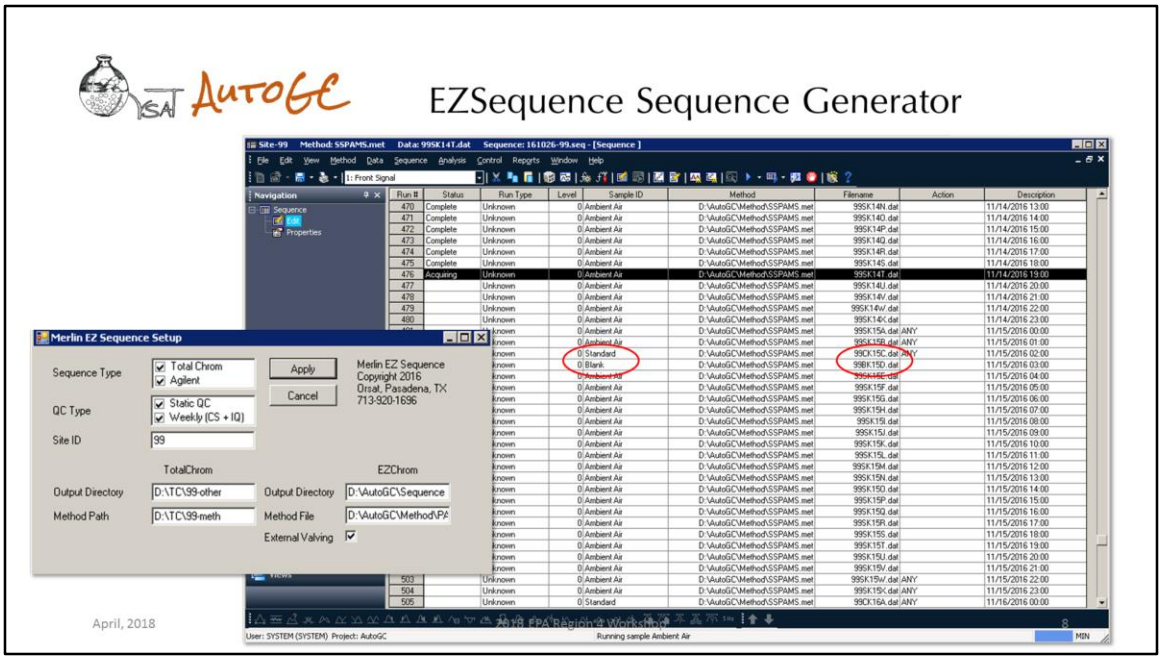
Key elements of the chromatographic method includes the Peaks and Groups table and Integration events.

The Peaks and Groups table allows the entry of

1. The component name
2. Retention time window
3. And Response Factor

The Integration Event table allows the introduction of

1. Width and threshold events as well as integration on/off



The sampling is scheduled using a sequence which is generated using the

1. Merlin EZ Sequence program. This program generates a text file which when loaded into the EZChrom sequence includes
2. routine QC samples, provides filenames which identify samples and the necessary valving events to control the introduction of samples.

EZSequence Sequence Generator

EZChrom Data Files

ASK25A.dat

- Site
- Sample type
- month
- day
- hour

Site designation: up to 3 alpha-numeric characters
Sample type: S = ambient; C = CVS; B = Blank; E = LCS; Q = RTS; D = MDL; M = multipoint
Month: A = Jan; B = Feb ..... L = Dec
Day: day-of-month
Hour: A = 00, B = 01, C = 03 .... X = 23

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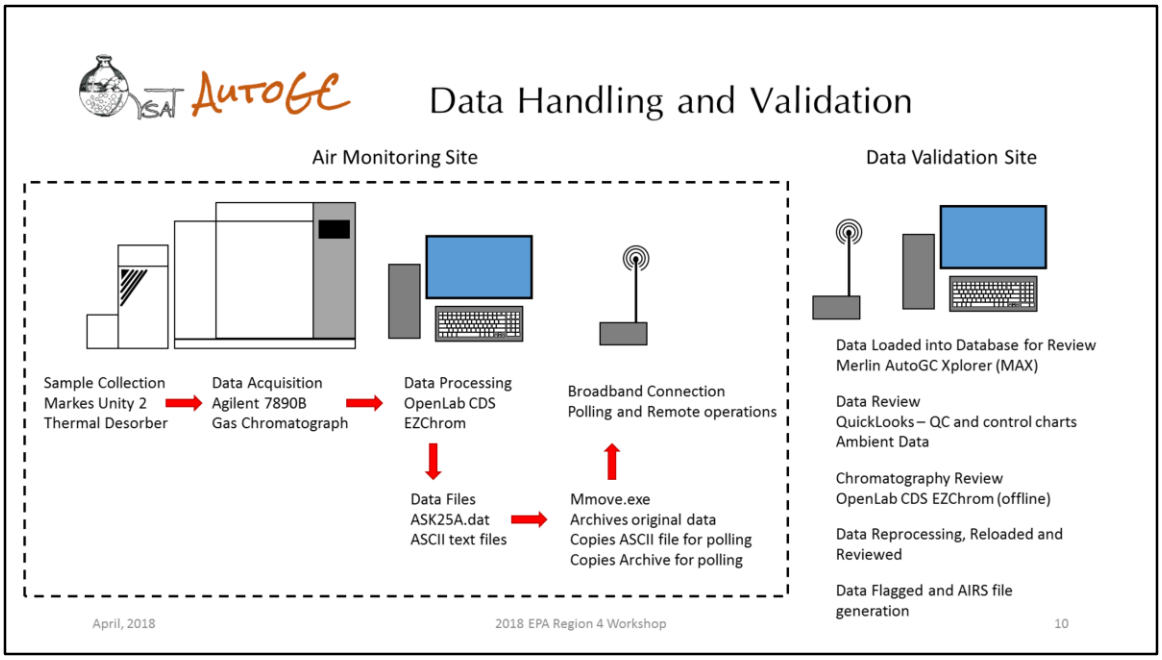
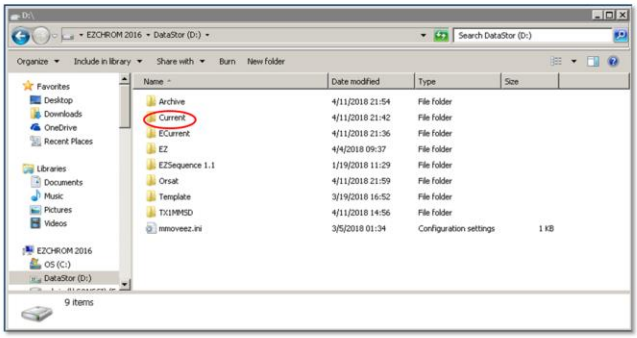
Filenames generated by EZSequence allow sorting of data and easy identification of site and sample type as well as month, day and hour of the day the sample was collected.



This shows a schematic representation of the system hardware and the process of sample collection and analysis. We supply and additional application which will automatically move data for polling and archive into zip files data to keep data organized and reduce losses.

1. In addition, it shows the flow of data from the chromatographic system to a remote site where data can be uploaded to our cloud-based system MAX and evaluated using MAX Quicklooks and graphic capabilities. If necessary, chromatographic data can be reprocessed and reloaded into MAX to correct any integration or identification issues which might arise. The ability to flag data and generate AIRS files is currently under development.

Data Handling and Validation



Setup File Structure for automatic archiving, polling and easy access

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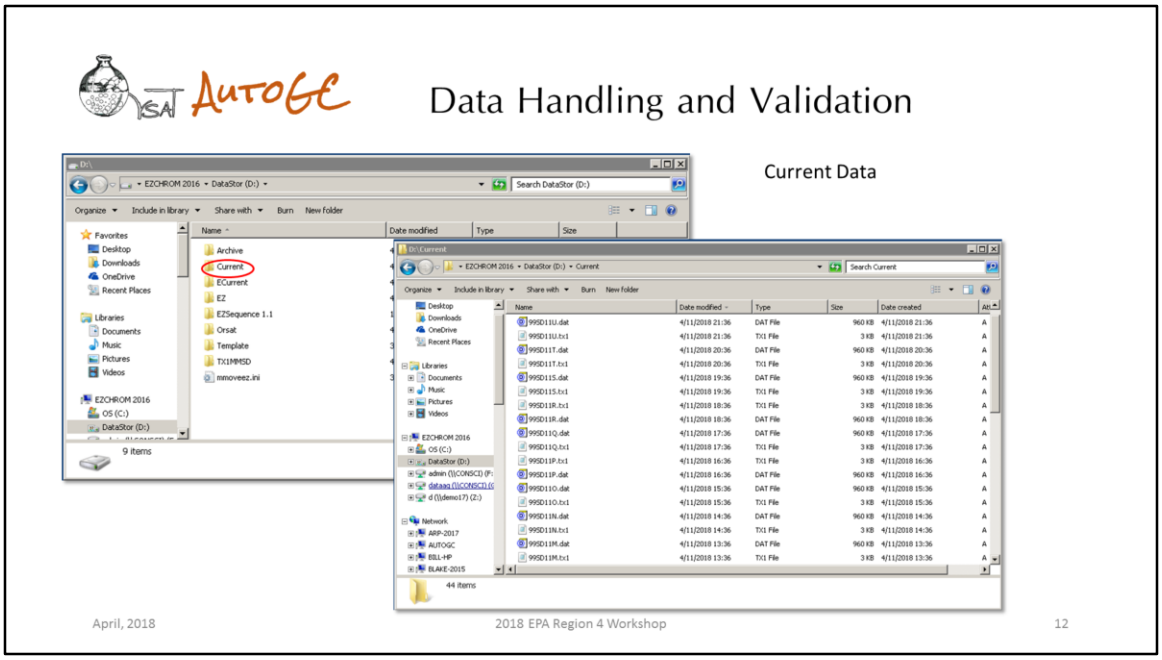
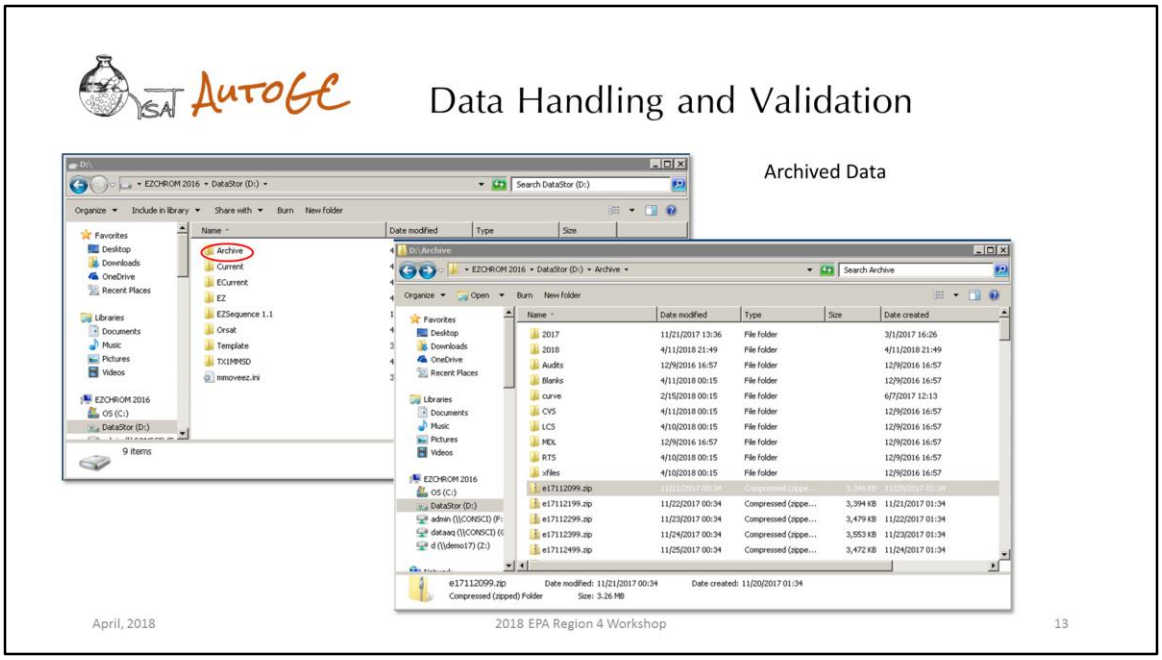
We will structure the data collection and archiving for remote access, polling and to make data easily accessible to operators.

1. The current directory will be where the data is written by EZChrom for the current day.



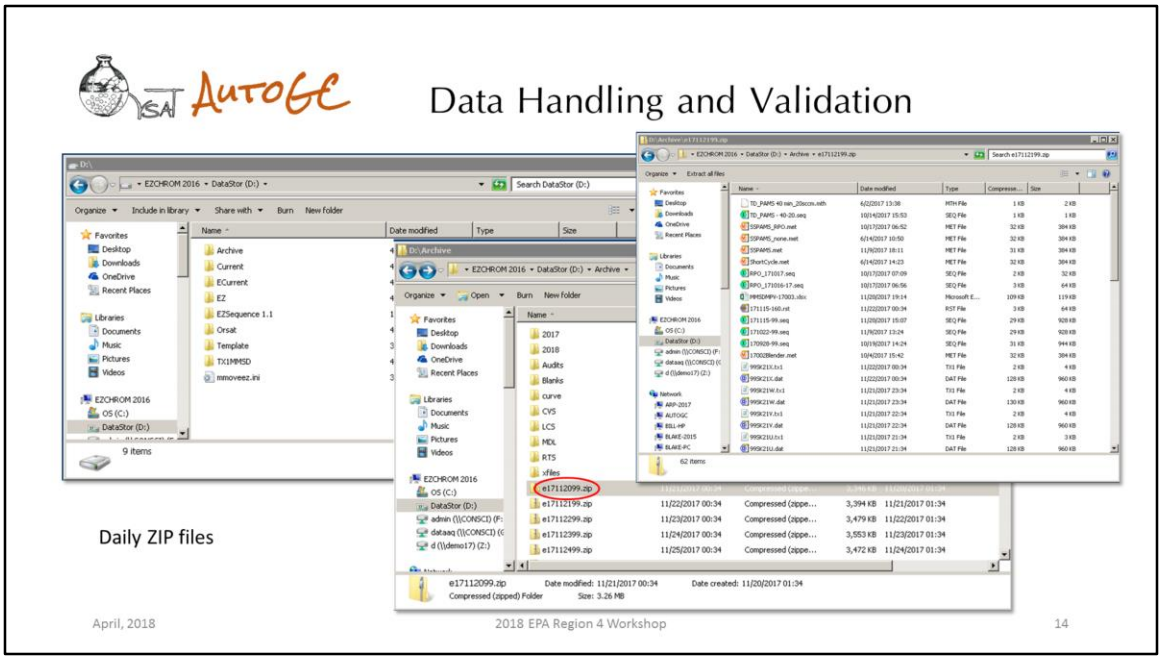
The current directory will contain the

1. raw data files and the ASCII text report files.

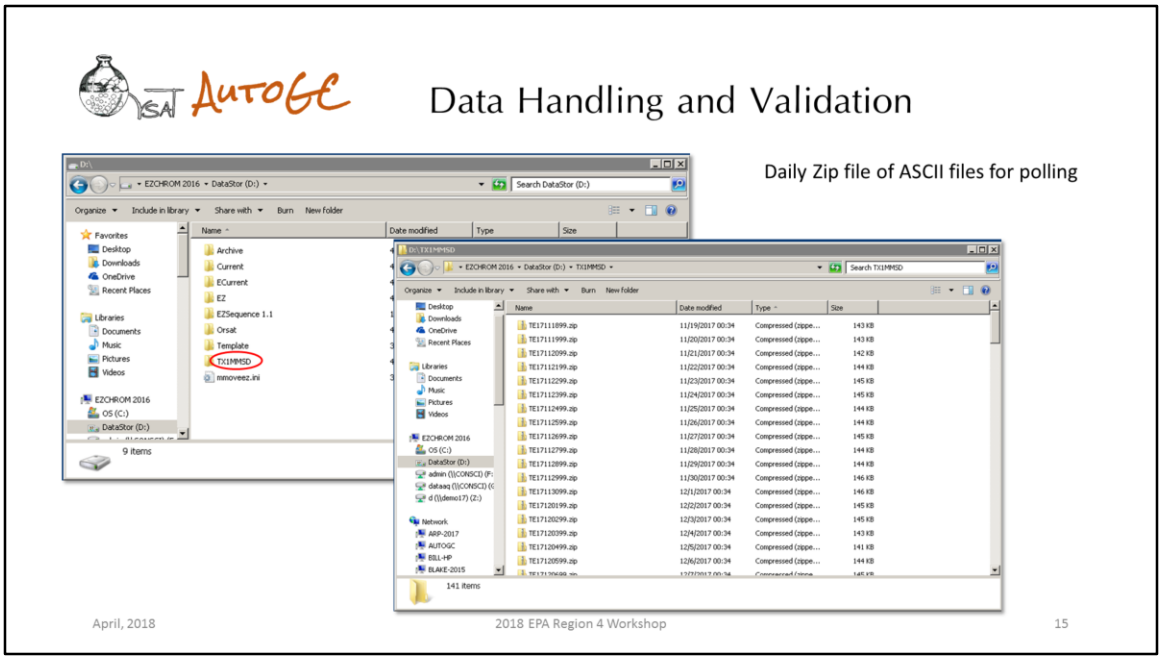


An Archive directory will contain the archived data.

1. Each day a zip file is written containing the data file and ASCII text report files and named for the site and date. Additional folders are in the archive folder which allow the automatic extraction of copies of the QC samples each day so they are always available to operators for review.



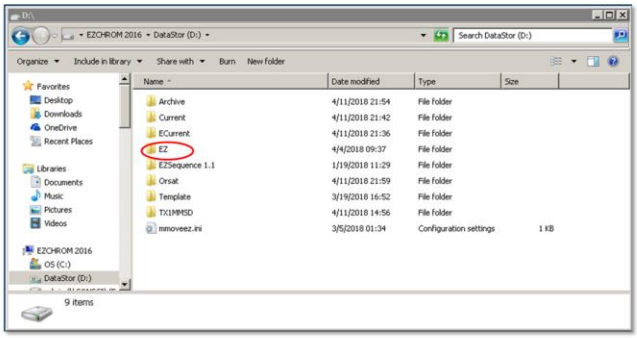
1. The Daily ZIP files also contain the contents of the
2. EZChrom method directory so validators will have copies of the blender spreadsheets and methods and sequences used in that day's analysis.



An additional folder is setup to allow the

1. generation of daily zip files of the ASCII text report files to allow for separate polling of just the report information

Data Handling and Validation



Separate directory for EZChrom method files which are archived with each daily zip file

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A separate fold holds the methods used by EZChrom to process all the data. Dilution system spreadsheets as well as logbooks are included in this directory so they will be included in the daily zip files of data.

Field Qualification Specifications

- Calibration Verification Standard (CVS - CCV) - Daily
  - Propane and Benzene ± 30%
  - All other components ± 30%
- Laboratory Check Standard (LCS - SSQC) – weekly
  - Propane and Benzene ± 30%
  - All other components - detected
- Blanks (SB) - Daily
  - No target > 0.5 ppbC
  - TNMHC < 10 ppbc total for both columns
- Retention Time Standard (RTS) – weekly
  - All targets identified
- Precision - %RPD < 20% - weekly

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This is an example of the quality control limits used for the week long field qualification.

Initial Calibration - ICAL

Calibration Curves – Initial Rubidoux

Calibration Curve Response Factors **Rubidoux**

Date: 7/9/2017
OP Aplummer

Plot RF	15601	4.7	%RSD
BP RF	13096	13.2	%RSD

Level		Zero psig.	Span psig.
		40	5
1	Blue		0.00097
2	Red		0.00542
3	Green		0.04406
4	Yellow		0.14861

	Standard Concentration ppbv	Level	File Name	Theoretical Concentration ppbc		Response Factor	Average Response Factor			R	all data points y-intercept area	conc ppbc	Predicted Value	% of Theoretical
Plot Column - Propane	1040	1	RUmG09B	3.02	50411	16702							3.26	108.0%
		2	RUCG09C	16.92	258620	15288	15471						16.72	98.8%
		3	RUmG09D	137.47	2058313	14973	4.7	%RSD	<10%	1.000	6647.80	0.43	133.04	96.8%
		4	RUmG09E	463.65	6918719	14922							447.20	96.5%
BP1 Column - Benzene	1090	1	RUmG09B	6.33	101484	16040							7.75	122.5%
		2	RUCG09C	35.46	448094	12637	13096						34.22	96.5%
		3	RUmG09D	288.16	3404054	11813	13.2	%RSD	<10%	1.000	15481.27	1.18	259.93	90.2%
		4	RUmG09E	971.89	11559268	11894							882.66	90.8%

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Orsat and Markes setup a system at SCAQMD which operated for about 6 weeks. This is an example of the calibration we generated at the beginning of the field study. Note we had benzene contamination which plagued this study for the duration although it reduced over time it adversely affected the QC data and calibration. The benzene in the blanks was from 2 ppbC and deteriorated over time. However it is significant to note that this did not appear to affect the ambient data as levels as low as 0.1 ppbC of benzene were routinely monitored. The contaminant was eventually isolated to a zero air line supplying the dilution system. It is also notable that in the initial calibration the lowest data point at nominally 1 ppbV showed a significantly higher response factor for both propane and benzene.

Final Calibration

Calibration Curves – Final Rubidoux

Calibration Curve Response Factors **Rubidoux**

Date: 8/13/2017
OP Aplummer

Plot RF	15537	2.6	%RSD
BP RF	13676	7.2	%RSD

Level	Zero psig.	Span psig.
	40	5
1	Blue	0.00097
2	Red	0.00542
3	Green	0.04406
4	Yellow	0.14861

	Standard Concentration ppbv	Level	File Name	Theoretical Concentration ppbc		Response Factor	Average Response Factor			R	all data points y-intercept area	conc ppbc	Predicted Value	% of Theoretical
Plot Column - Propane	1040	1	RUcH13M	3.02	48771	16159							3.14	104.0%
		2	RUmH13N	16.92	263393	15570	15537						16.95	100.2%
		3	RUmH13O	137.47	2068330	15045	2.6	%RSD	<10%	1.000	9843.48	0.63	133.12	96.8%
		4	RUmH13P	463.65	7128114	15374							458.78	98.9%
BP1 Column - Benzene	1090	1	RUcH13M	6.33	97172	15359							7.11	112.3%
		2	RUmH13N	35.46	474425	13379	13676						34.69	97.8%
		3	RUmH13O	288.16	3746817	13002	7.2	%RSD	<10%	1.000	15481.27	1.13	273.98	95.1%
		4	RUmH13P	971.89	12597570	12962							921.17	94.8%

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The calibration runs at the end of the field study were significantly better RSDs across response factors for both propane and benzene although there was still a significant contribution from the benzene contaminant.

Final Calibration

Calibration Curves – Final Rubidoux

Calibration Curve Response Factors **Rubidoux**

Date: 8/13/2017
OP Aplummer

Plot RF	15591	2.9	%RSD
BP RF	13914	7.4	%RSD

Level		Zero psig.	Span psig.
		40	5
1	Blue		0.00097
2	Red		0.00542
3	Green		0.04406
4	Yellow		0.14861

	Standard Concentration ppbv	Level	File Name	Theoretical Concentration ppbc		Response Factor	Average Response Factor			R	y-intercept area	conc ppbc	Predicted Value	% of Theoretical
Plot Column - Propane	1040	1	RUcH13M	3.02	48771	16159							3.13	103.6%
		2	RUmH13N	16.92	263393	15570	15591						16.89	99.9%
		3	RUmH13O	137.47	2068330	15045	2.9	%RSD	<10%	1.000	6391.67	0.41	132.66	96.5%
		4	RUmH13P	463.65	7128114	15374							457.18	98.6%
BP1 Column - Benzene	1090	1	RUcH13M	6.33	97172	15359							6.98	110.4%
		2	RUmH13N	35.46	474425	13379	13914						34.10	96.2%
		3	RUmH13O	288.16	3746817	13002	7.4	%RSD	<10%	1.000	29984.38	2.16	269.29	93.5%
		4	RUmH13P	971.89	12597570	12962							905.42	93.2%

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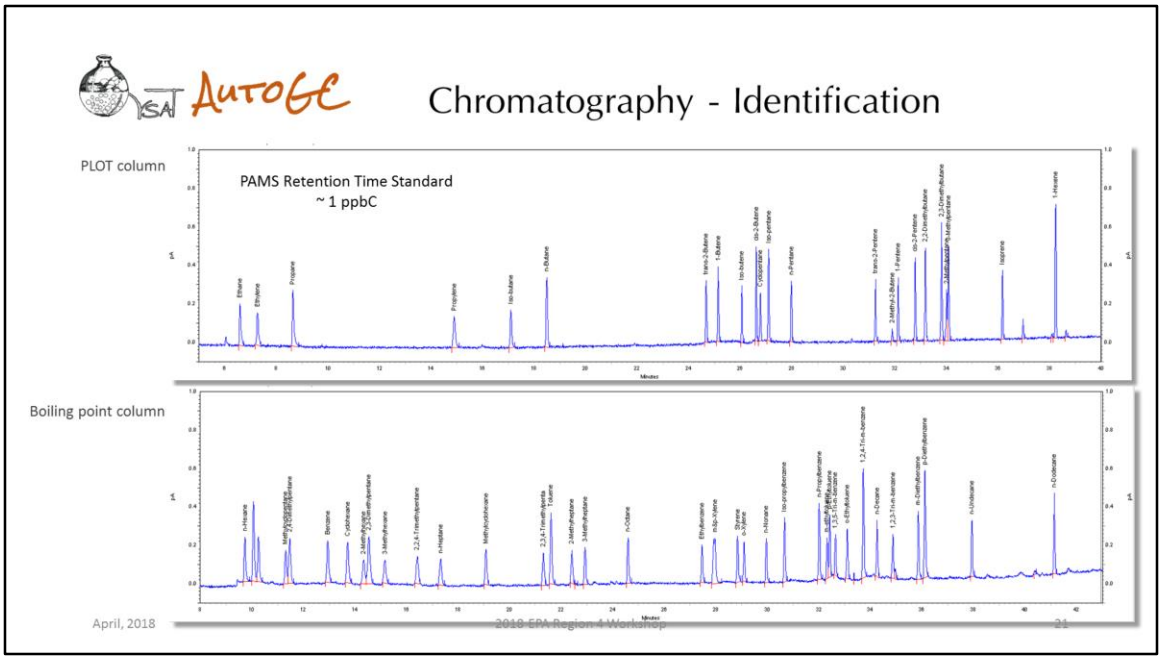
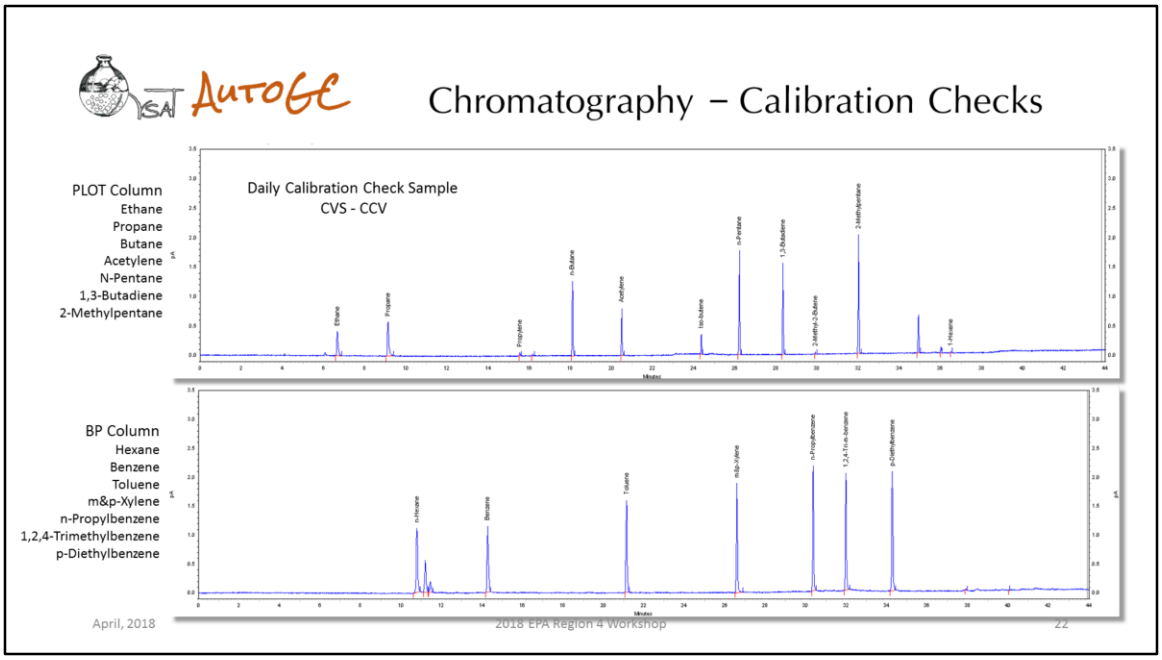
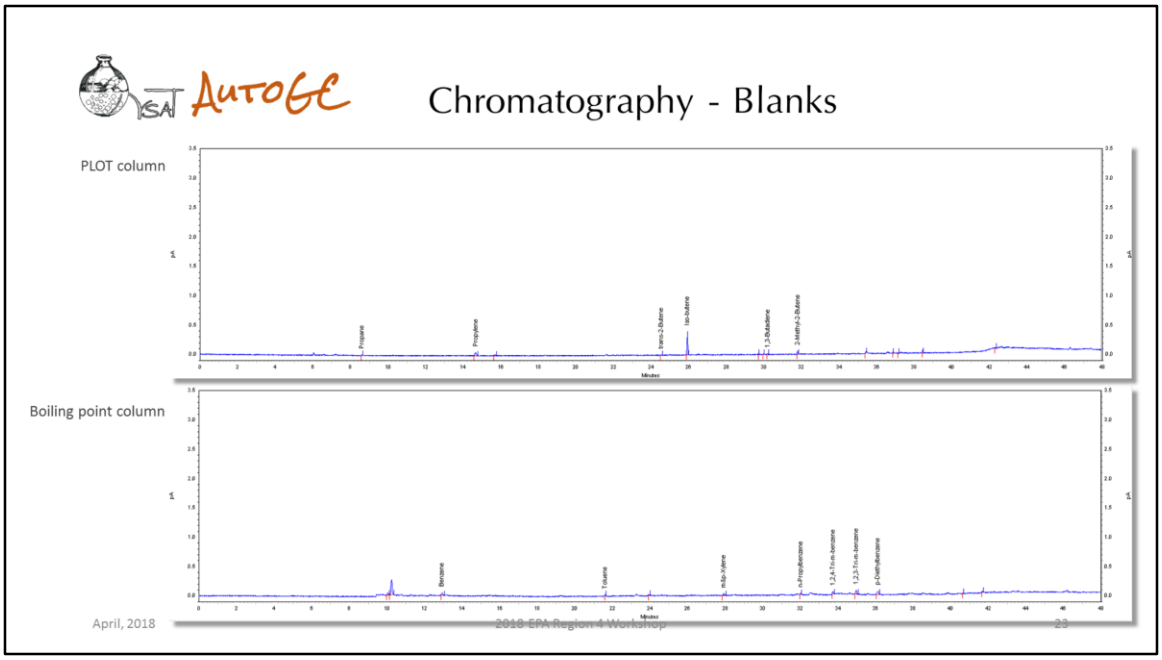
Since the range of this curve far exceeds potential ambient levels we calculated RSDs on only the lowest points. The FID is extremely linear and even on the higher RSD curves we never saw R values of anything but 1 and the variation of Response factors was not significant for the lowest point and was reduced over the course of the trial.



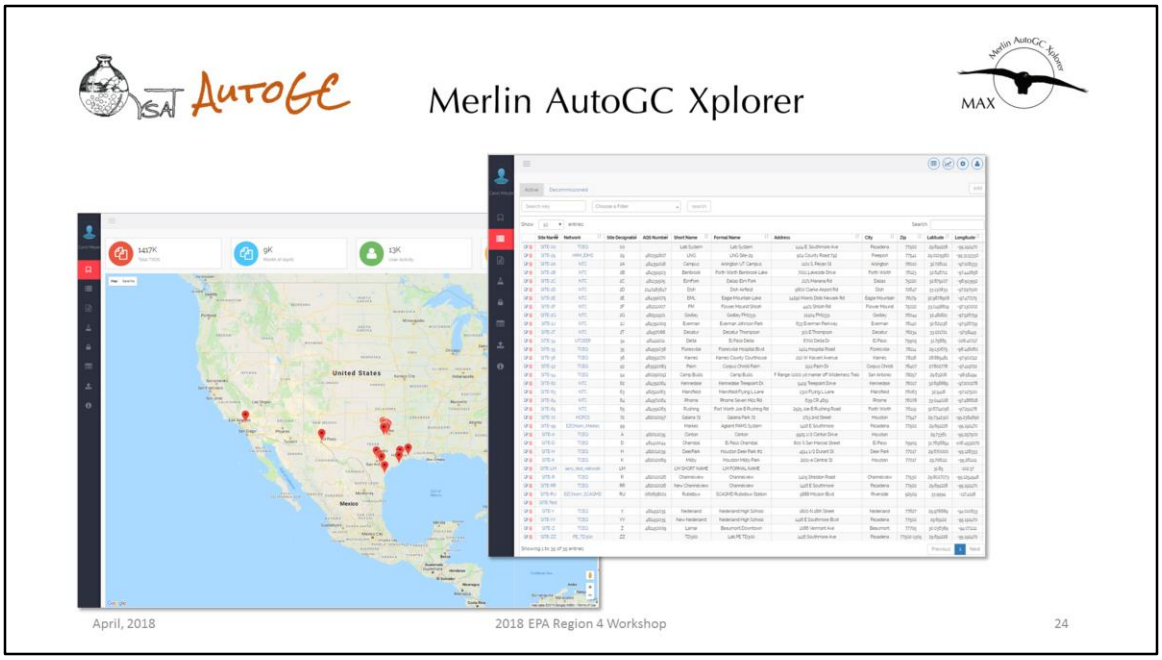
This is a chromatogram of the PAMS standard diluted to nominally 1 ppbC by partial injection of the PAMS standard followed by humidified zero air.



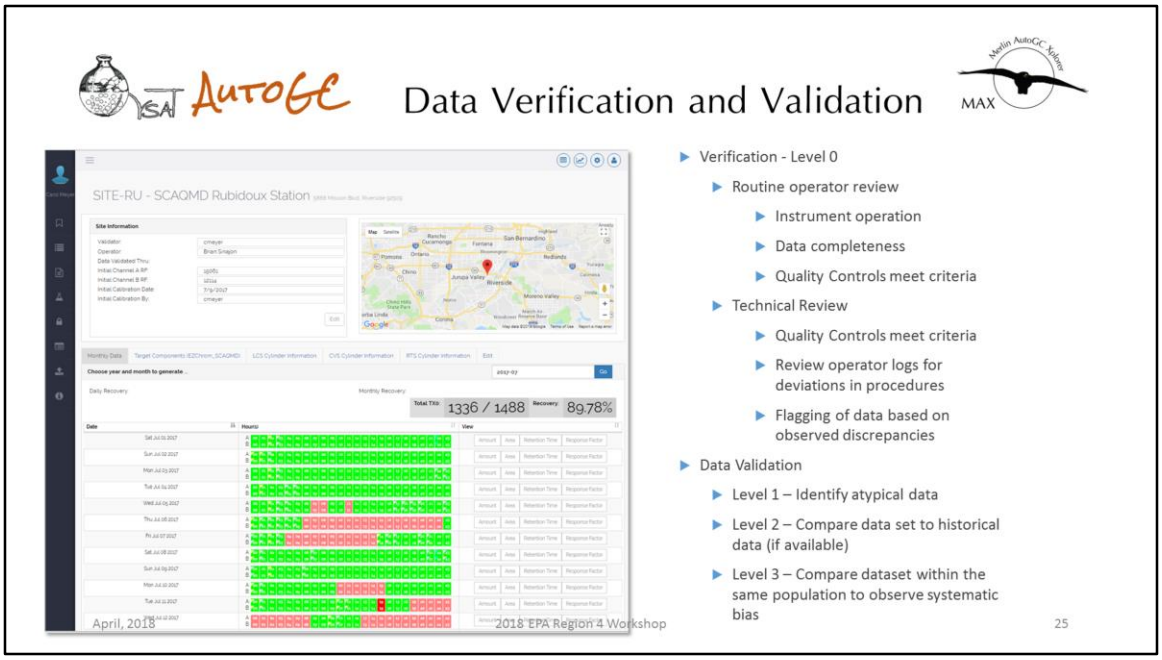
CVS – Calibration Verification Standard
CCV – Continuing Calibration Verification



Method Blank – which is humidified diluent gas from the dilution system



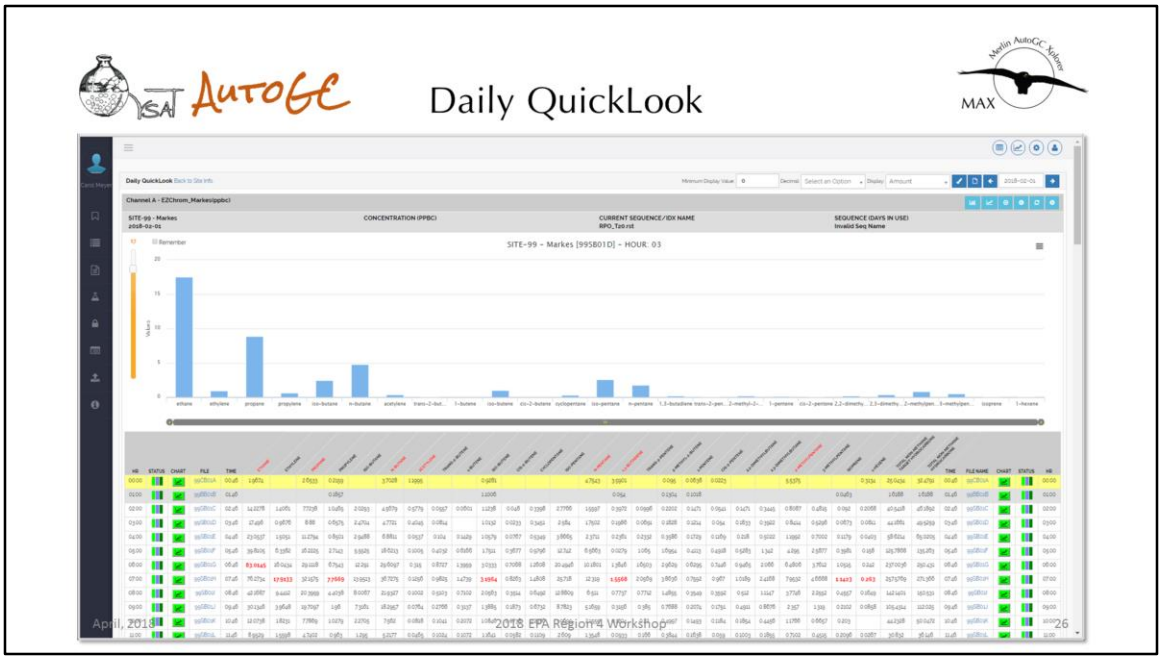
Orsat has developed a cloud-based database for the review of AutoGC data called the Merlin AutoGC Xplorer or MAX. It was specifically developed because other existing systems did not adequately allow the review of QC data, generation of control charts and easy identification of data not meeting data quality objectives. MAX not only allows for tracking quality control data it also allows configuration of networks with differing pass/fail criteria as well as tracking of calibration standards over time.



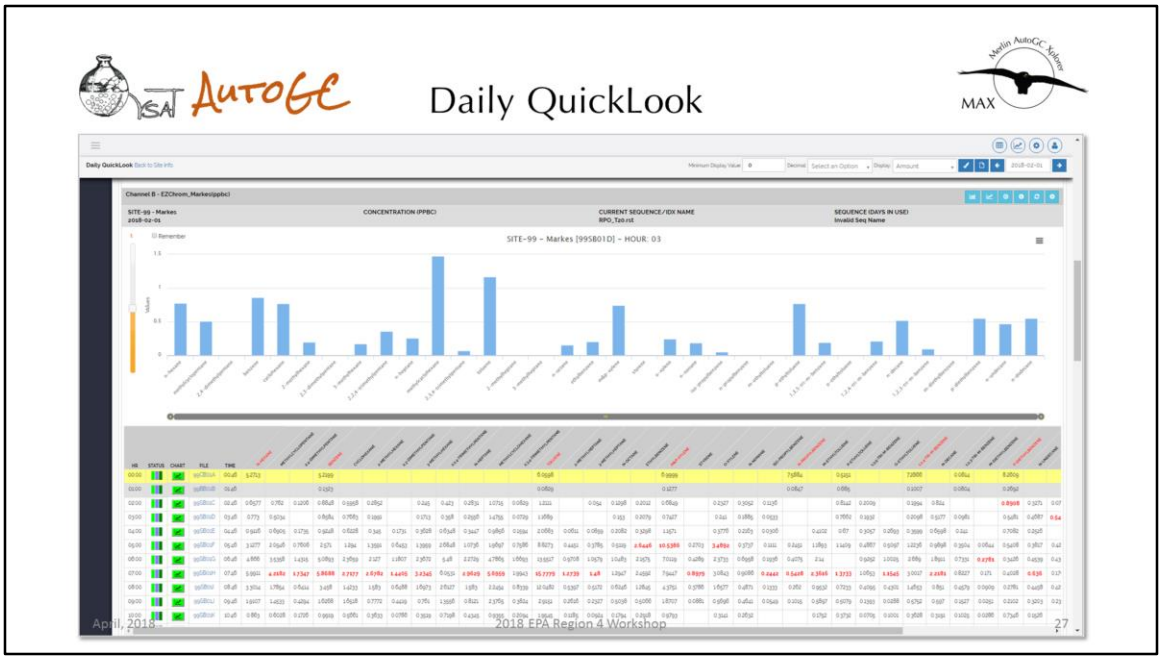
MAX can facilitation PAMS VOC data verification and Validation which is broken into several levels

1. Verification includes routine
    - operator review for general instrument operation, data completeness and pass/fail criteria for QC samples
    - And Technical review by technical staff of QC data, operator logs for deviations and well as flagging
2. Validation is broken into several levels and focuses on review of ambient data for outliers and comparison with historical data where it exists.

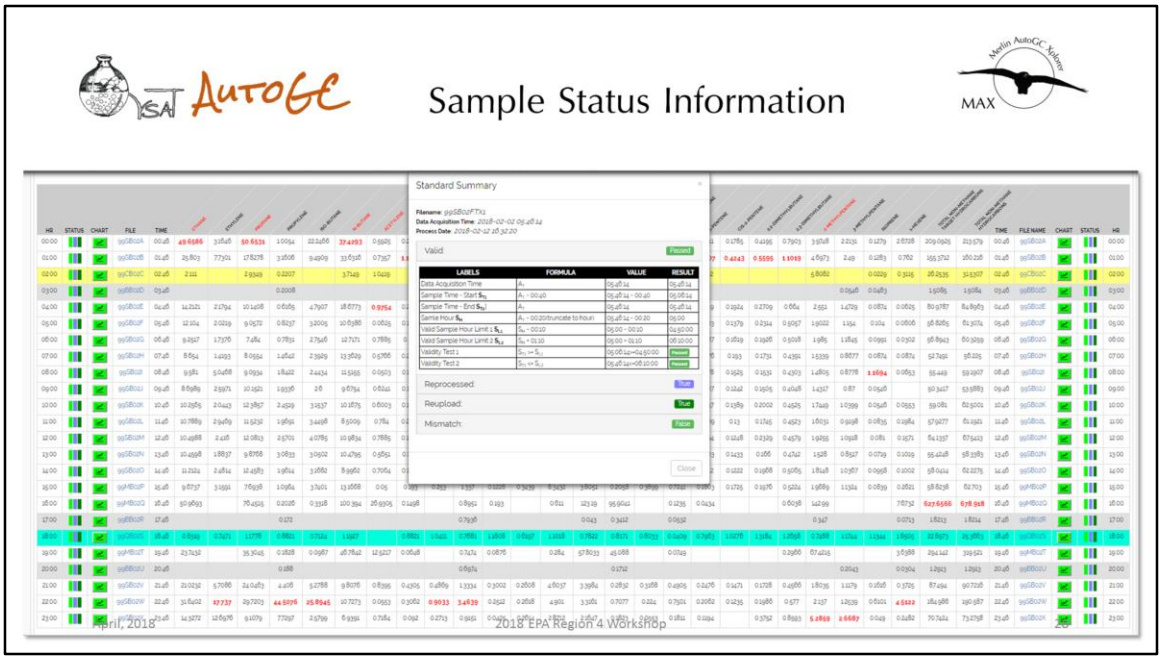
MAX shows missing data as well as data collected but not valid due to timing issues and calculates data completeness



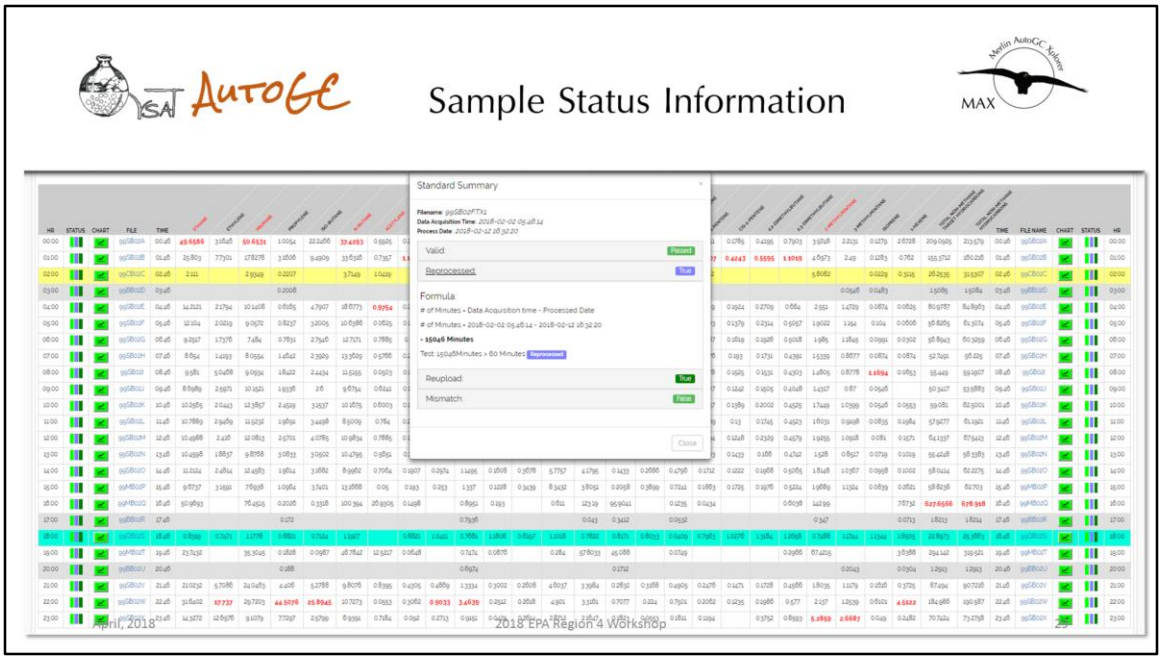
The Daily QuickLook by amount shows the ppbC amount of all samples as well as a bar-chart representation of each sample. This is data for the light gases on the PLOT column. High values for each hour are highlighted.



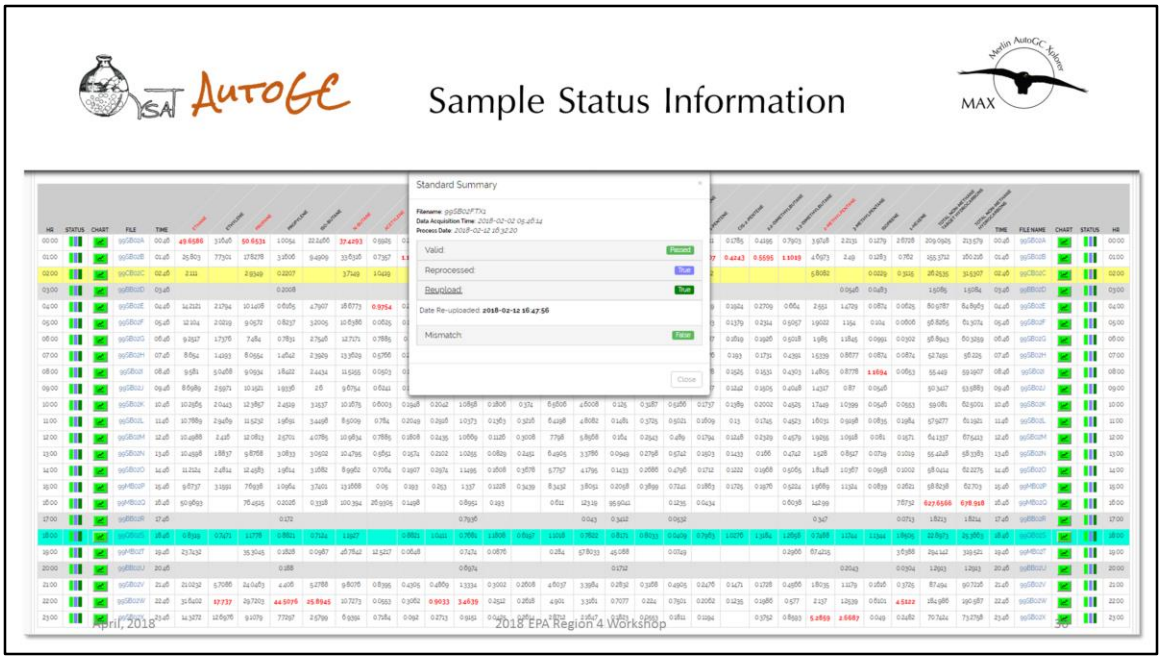
Scrolling down on the QuickLook shows results from both chromatographic columns. This is the C6+ data. Filenames link directly to the information from each ASCII text file which was ingested into the system.



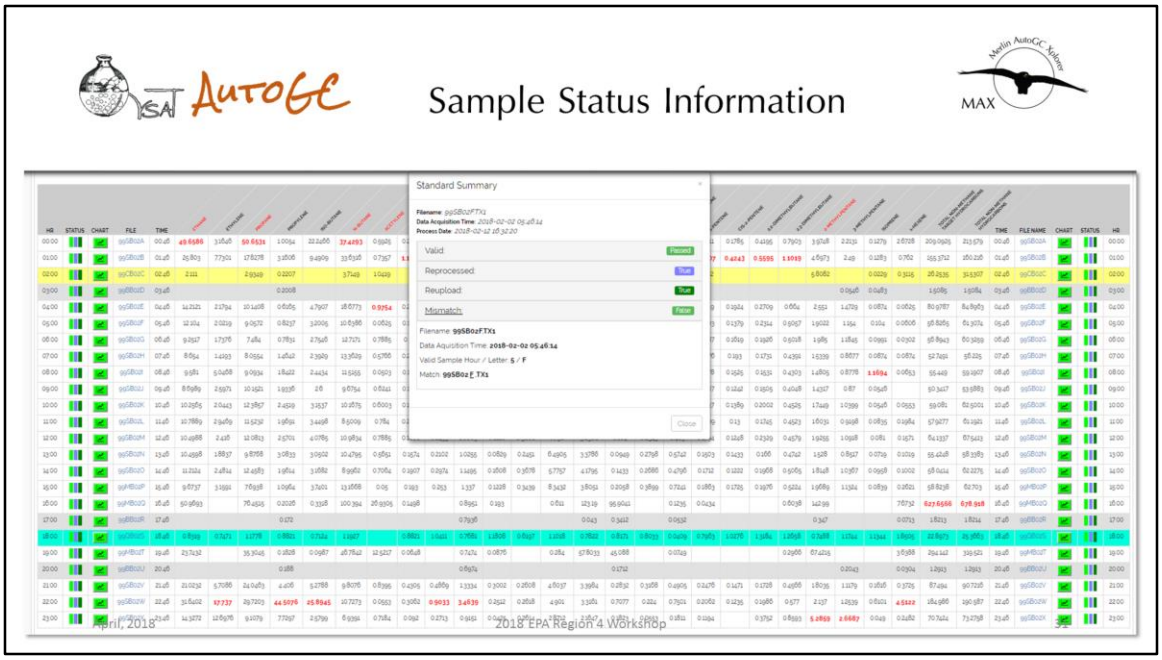
Status flags show details of each sample hour loaded such as Validity based on timing – this shows the calculation of the sample time from the data acquisition time from the chromatographic data system. If the sample time is outside the +/- 25% criteria the data will be flagged as invalid.



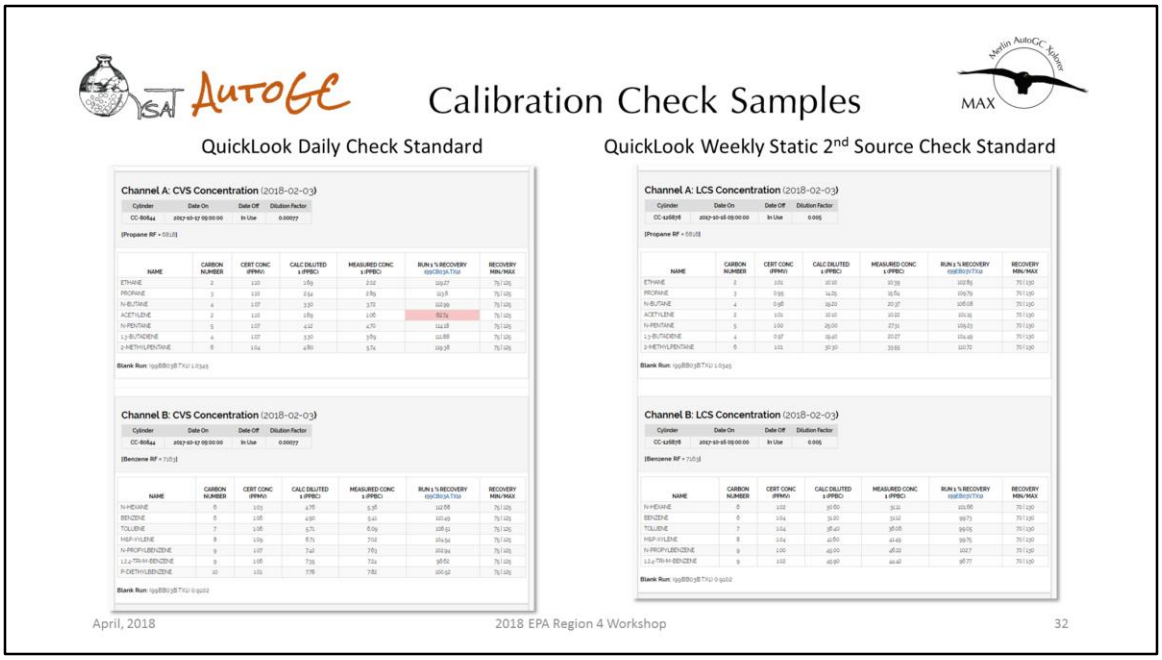
Additional status flags include whether or not the data was reprocessed



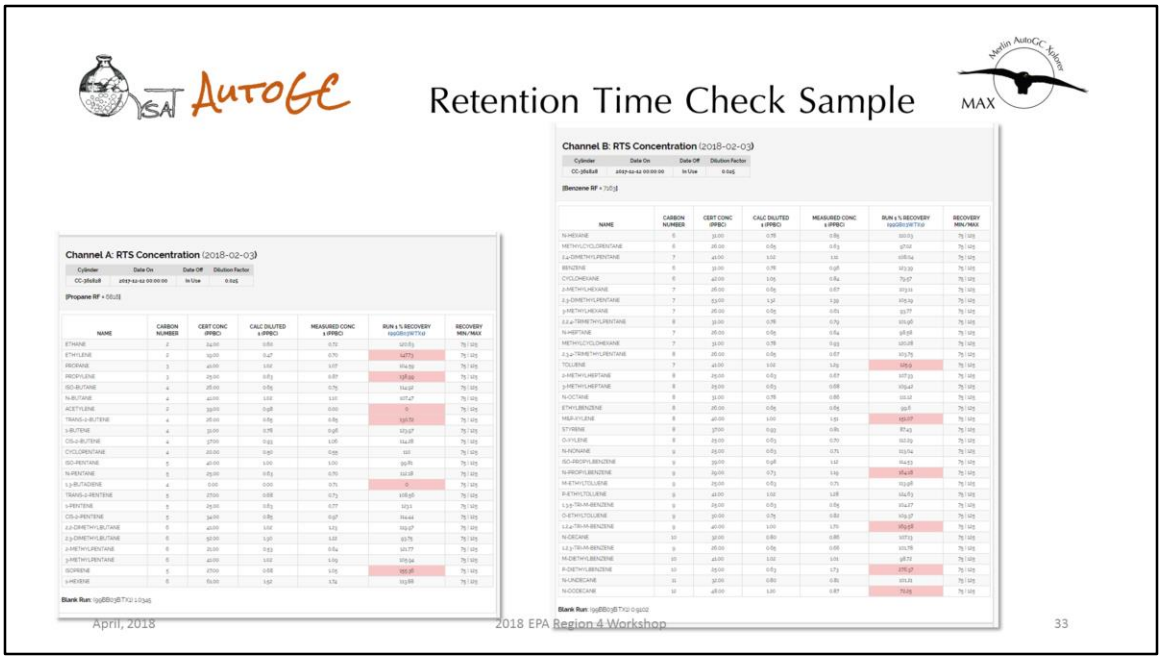
If the data was re-uploaded



And if the filename does not match the actual acquisition time – which can occur if the system sequence has drifted off time due to sampling issues.



Below the Quicklook the daily QC sample recoveries are calculation so operators can have immediate pass/fail information. This shows both the daily CVS recoveries based on +/- 25% criteria and weekly second source standard recoveries based on +/- 30% Recoveries.



If a retention time standard was run and a dilution supplied in the network setup the Quicklook will calculate the recoveries of this standard as well.

Daily Blanks

Channel A: BLANK Concentration (2018-02-03)

NAME	RUN 1 (PPBC) AMOUNT (pp88ro38.TXp)	MAX
PROPYLENE	0.3583	0.5
1-PENTENE	0.0409	0.5
3-METHYLBENTANE	0.0349	0.5
CHANNEL A TNMTC	0.2587	

Channel B: BLANK Concentration (2018-02-03)

NAME	RUN 1 (PPBC) AMOUNT (pp88ro38.TXp)	MAX
TOLUENE	0.0490	0.5
M&P-XYLENE	0.0753	0.5
N-PROPYLBENZENE	0.0044	0.5
1,2,4/1,3-M-BENZENE	0.0755	0.5
P-DIETHYLBENZENE	0.4060	0.5
CHANNEL B TNMTC	0.9402	

TOTAL BLANKS (TNMTC)

	RUN 1 (PPBC) AMOUNT (pp88ro38.TXp)
TNMTC CHANNEL A:	0.2587
TNMTC CHANNEL B:	0.9402
TOTAL TNMTC:	1.1789

TOTAL BLANKS (TNMHC)

	RUN 1 (PPBC) AMOUNT
TNMHC CHANNEL A:	1.0345
TNMHC CHANNEL B:	0.9402
TOTAL TNMHC:	1.9947

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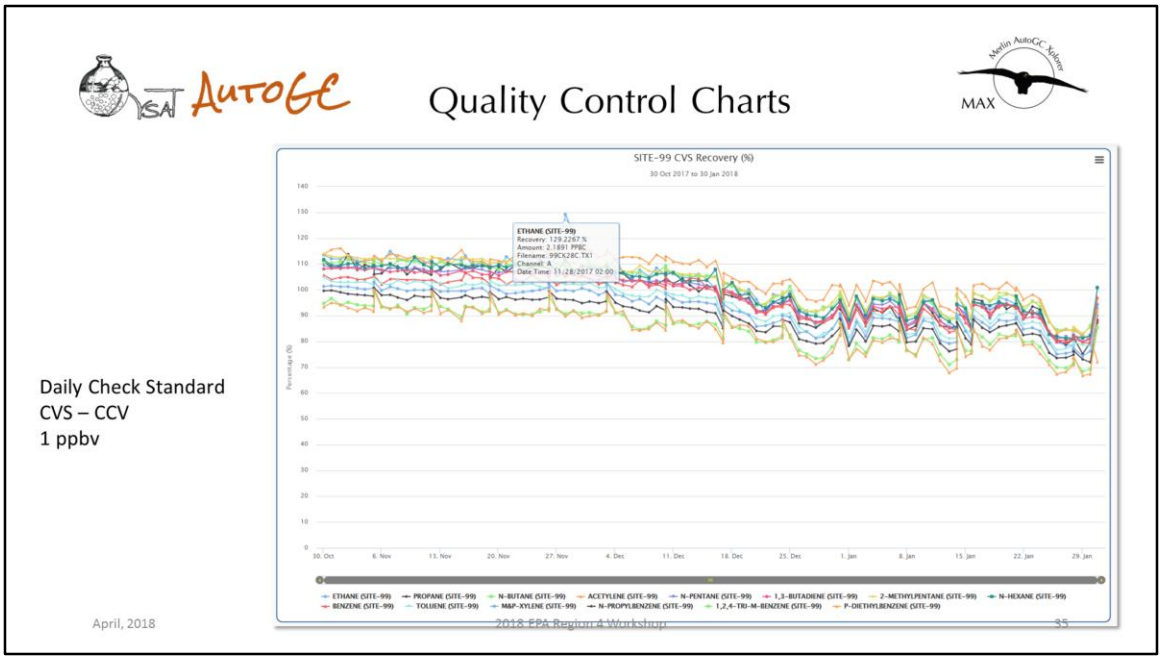
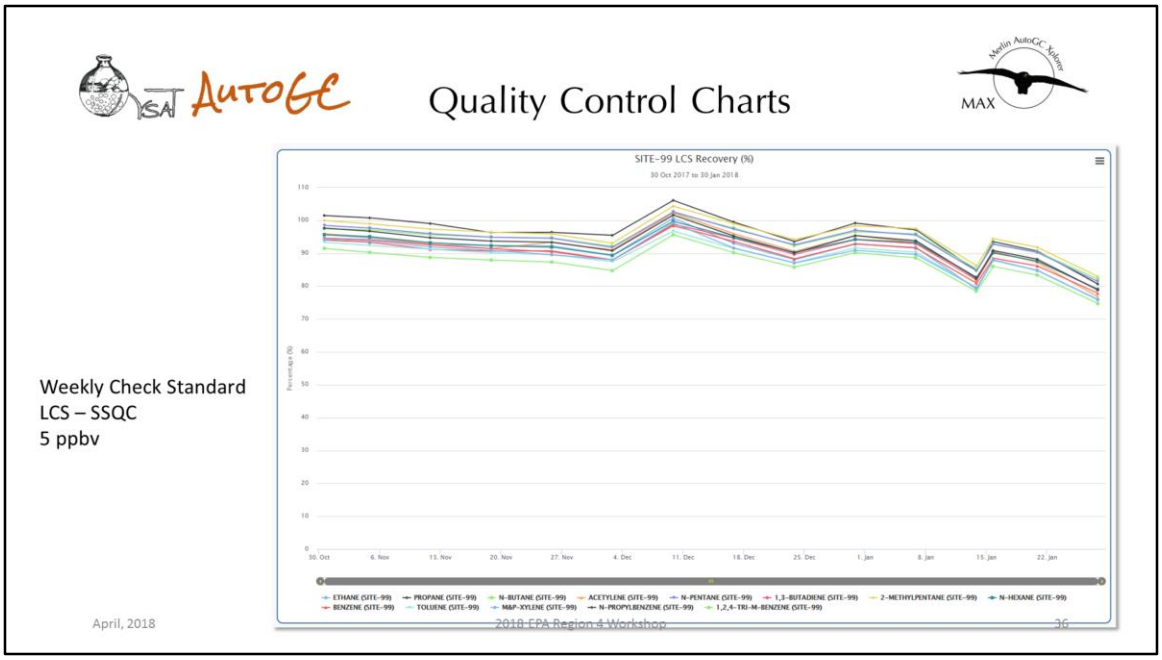
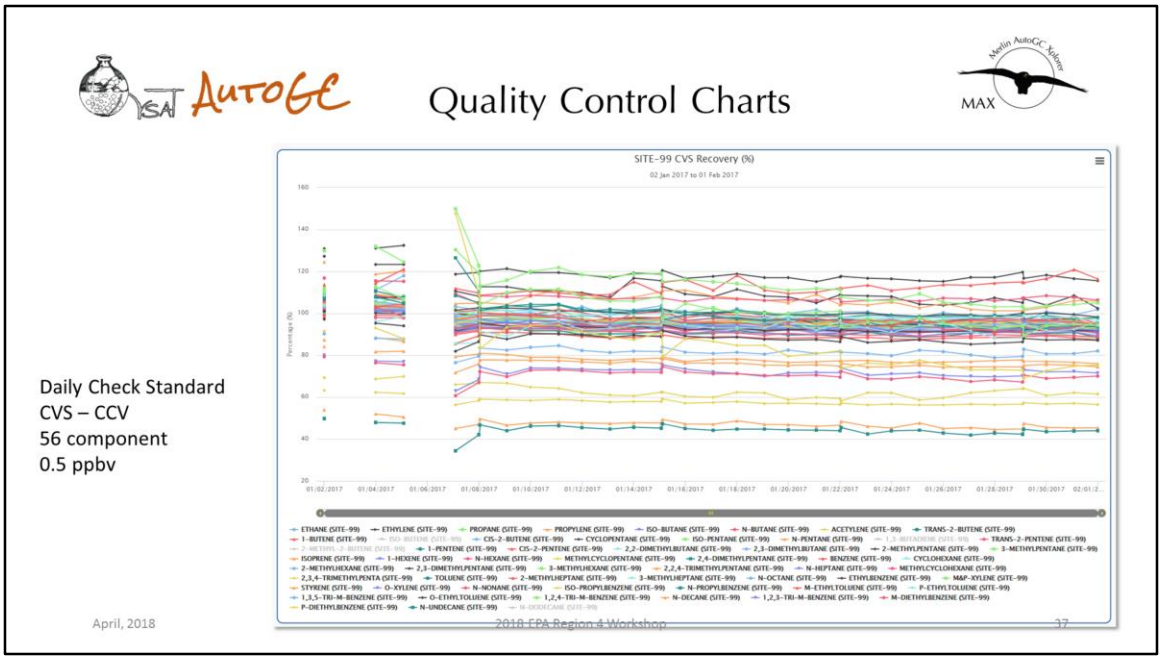
Daily blanks show any targets which occur in the daily blank and are highlighted based on the network pass/fail criteria. It also shows totals.



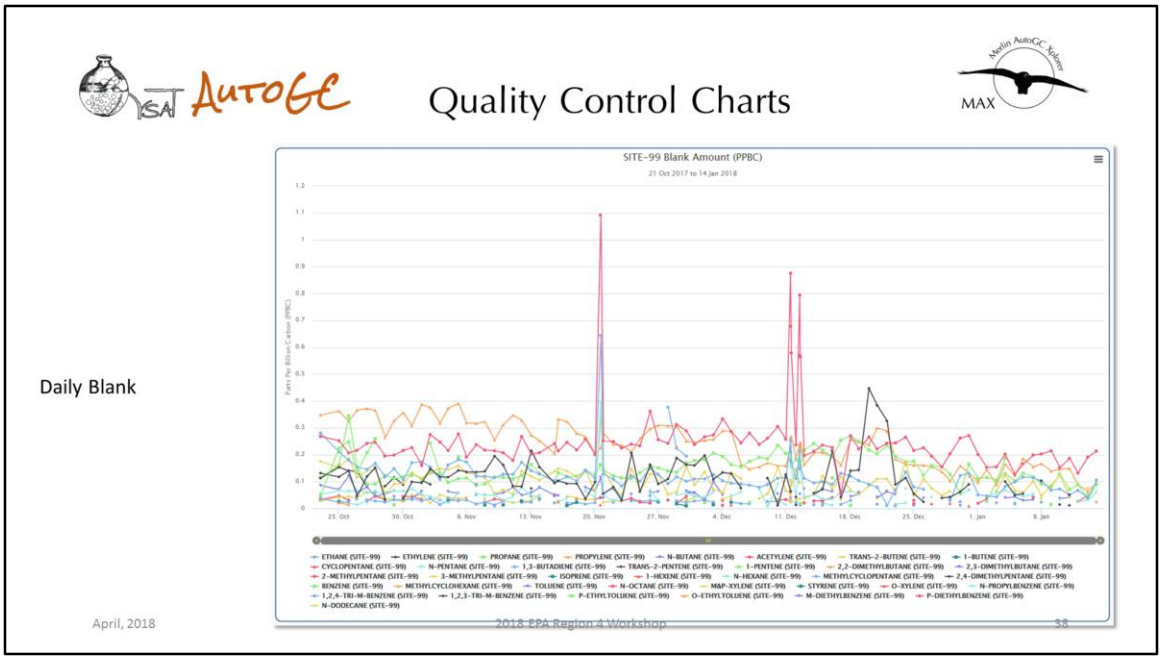
Unlike some other systems MAX was originally designed specifically to allow the charting of QC data. This is a graph of the nightly check sample over 4 months. MAX data supplies roll-over text which shows the recovery, amount, time and date as well as the actual filename so validators or operators can quickly locate the actual datafile for chromatographic review if necessary.



This is the control chart for the second source standard over the same time period.



Because MAX can be setup for variations in QC it is capable of allowing for nightly checks with all targets or only a limited number.



Blanks can also be charted across time.

Quality Control Charts

CSV or Excel output of graphed data

CSV Excel

Hide Data Table

DATE TIME	ETHANE (SITE-ppb) PPBC	ETHYLENE (SITE-ppb) PPBC	PROPANE (SITE-ppb) PPBC	PROPYLENE (SITE-ppb) PPBC	N-BUTANE (SITE-ppb) PPBC	ACETYLENE (SITE-ppb) PPBC	TRANS-2-BUTENE (SITE-ppb) PPBC	1-BUTENE (SITE-ppb) PPBC	CYCLOPENTANE (SITE-ppb) PPBC	N-PENTANE (SITE-ppb) PPBC	1,3-BUTADIENE (SITE-ppb) PPBC	TRANS-2-PENTENE (SITE-ppb) PPBC	1-PENTENE (SITE-ppb) PPBC	2,3-DIMETHYLBUTANE (SITE-ppb) PPBC	2-METHYLPENTANE (SITE-ppb) PPBC	3-METHYLPENTANE (SITE-ppb) PPBC	ISOPRENE (SITE-ppb) PPBC	1-HEXENE (SITE-ppb) PPBC	N-HEXANE (SITE-ppb) PPBC	METHYLCYCLOPENTANE (SITE-ppb) PPBC	2,4-DIMETHYLPENTANE (SITE-ppb) PPBC	BENZENE (SITE-ppb) PPBC	METHYLCYCLOHEXANE (SITE-ppb) PPBC	TOLUENE (SITE-ppb) PPBC	N-OCTANE (SITE-ppb) PPBC	M&P-XYLENE (SITE-ppb) PPBC	STYRENE (SITE-ppb) PPBC	O-XYLENE (SITE-ppb) PPBC	N-PROPYLBENZENE (SITE-ppb) PPBC	1,2,4-TRI-M-BENZENE (SITE-ppb) PPBC	1,2,3-TRI-M-BENZENE (SITE-ppb) PPBC	P-ETHYLTOLUENE (SITE-ppb) PPBC	O-ETHYLTOLUENE (SITE-ppb) PPBC	M-DIETHYLBENZENE (SITE-ppb) PPBC	P-DIETHYLBENZENE (SITE-ppb) PPBC	N-DODECANE (SITE-ppb) PPBC
10/21/2017 01:00		0.1312		0.3475		0.0326	0.0275				0.0378											0.1155		0.0855		0.1752			0.0527	0.2804	0.1128	0.0487			0.2680
10/23/2017 01:00		0.1173		0.3625		0.0468	0.0422			0.0308	0.0225							0.0247				0.1607		0.0704		0.1527			0.0658	0.2103	0.1535	0.2238	0.0209		0.2523
10/24/2017 03:00		0.1407		0.3241		0.0306	0.0444			0.0197	0.0235											0.3445		0.1234		0.1869			0.0639	0.1796	0.1391	0.2478	0.0134		0.2069
10/25/2017 01:00		0.1370		0.3653			0.0382			0.0130											0.0348	0.1521		0.0586		0.1149			0.0667	0.1551	0.0454	0.1346			0.2161
10/26/2017 03:00		0.0792		0.3720		0.0290	0.0624			0.0304	0.0318									0.0191		0.0899		0.0800		0.1408			0.0574	0.1454	0.1191	0.2075			0.2420
10/27/2017 01:00				0.3661		0.0451	0.0511				0.0276										0.0604	0.0910		0.0446		0.1452			0.0646	0.1672	0.1522	0.2594			0.2458
10/28/2017 03:00		0.0828		0.2643		0.0332	0.0364				0.0236											0.1229		0.0558		0.0542			0.0512	0.1172	0.0339				0.1950
10/29/2017 02:00		0.1157		0.3268	0.0431		0.0326				0.0325		0.0135									0.1107		0.0660		0.0910			0.0657	0.1479					0.1986
10/30/2017 03:00		0.0881		0.3585		0.0440	0.0247				0.0322											0.1170				0.0941			0.0630	0.1070	0.0367				0.2158
10/31/2017 01:00				0.3082		0.0450	0.0503				0.0362										0.0326	0.1303		0.0389		0.1311			0.0707	0.1701	0.0990	0.1220			0.2264

Showing 1 to 10 of 92 entries

Previous 1 2 3 4 5 .. 10 Next

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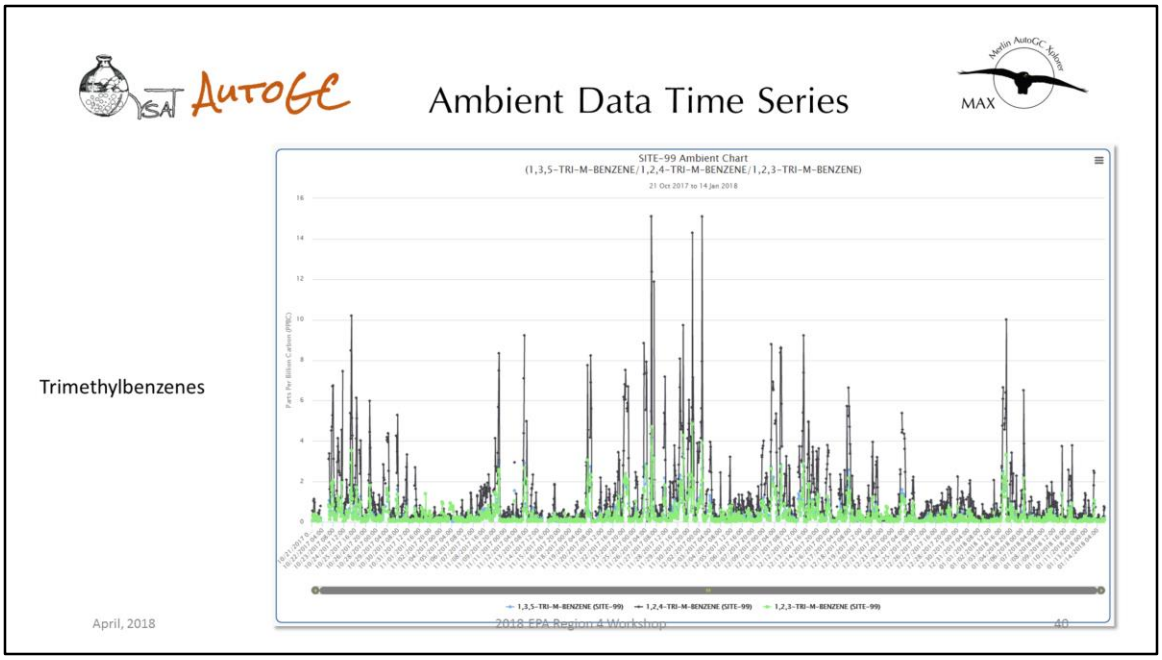
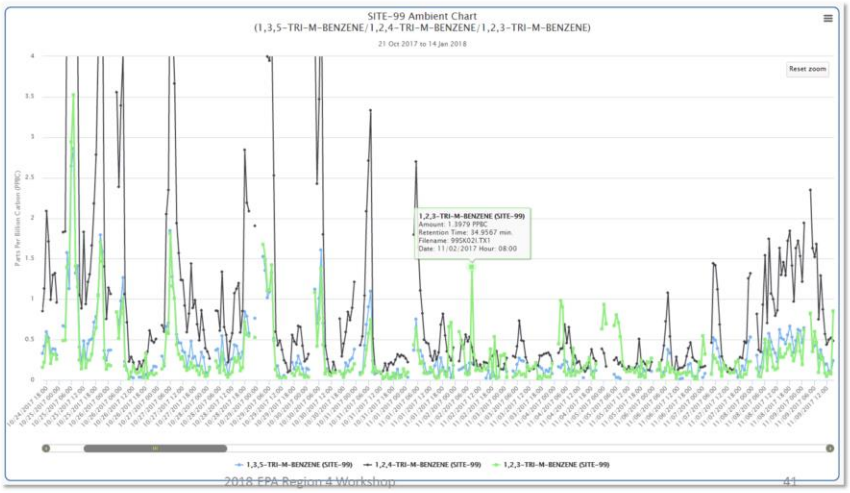
All charted data can be exported to csv or excel format. This is useful when attempting to generate MDLs using the new MUR requirements.



MAX can also facilitate validation of ambient air using time series.

Ambient Data Time Series

- Expand to inspect
- Locate outliers
- Identification of data file



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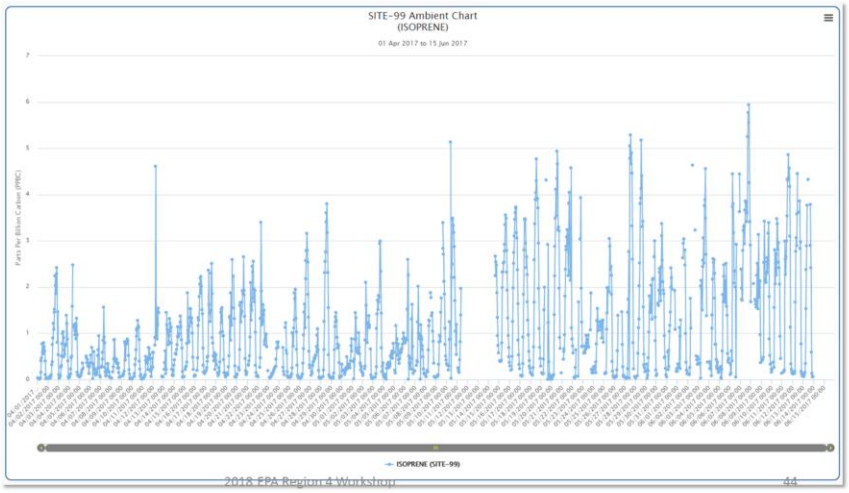
Time series of related species such at the trimethylbenzene can facilitate location of outliers and the actual datafiles associated with outlier data.

Ambient Data Time Series

Diurnal Patterns
Isoprene



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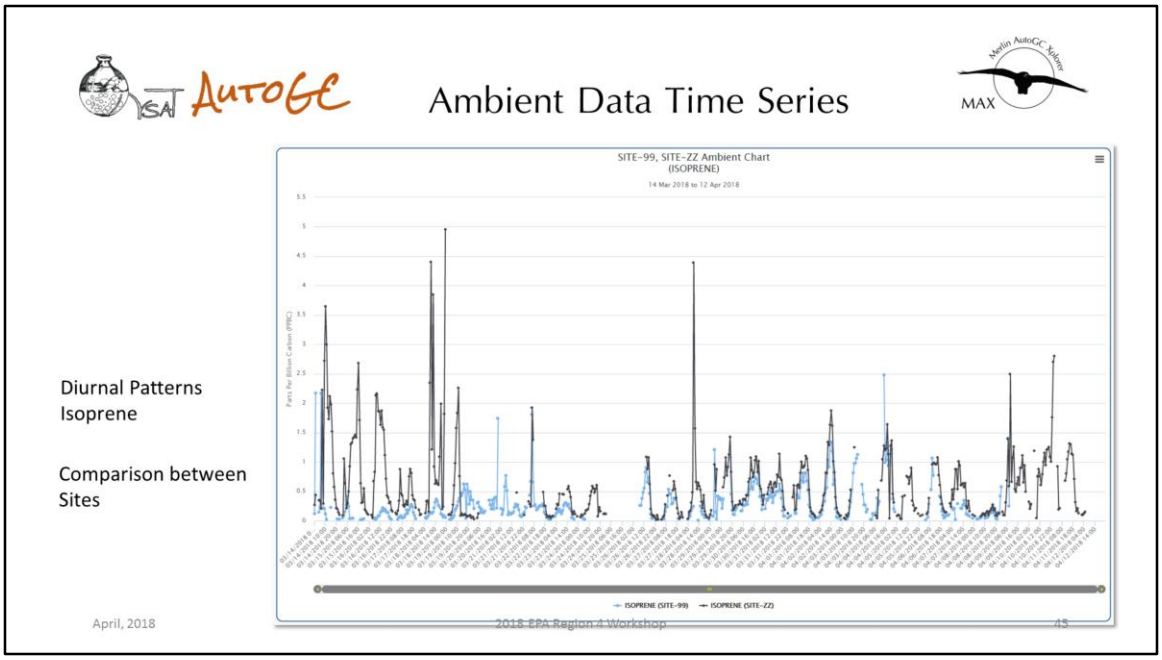
Time series can be used to review expected diurnal patterns for a single site or

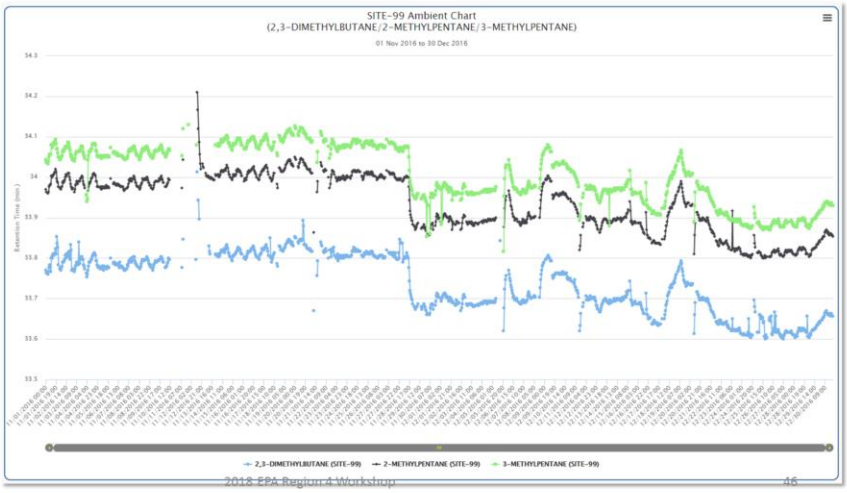


Or across multiple sites.

Ambient Data Time Series

Time Series of component retention times to identify missidentifications

Plot column
- 2,3-Dimethylbutane
- 2-Methylpentane
- 3-Methylpentane



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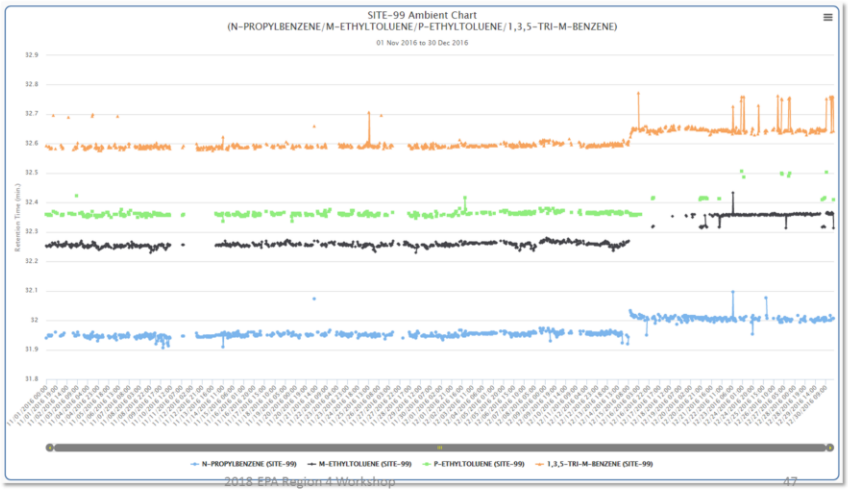
A unique feature of MAX is the ability to graph the retention times of targets. This is helpful to review closely eluting peaks such as the methylpentanes at the end of the PLOT column. This will show potential misidentifications.

Ambient Data Time Series

Time Series of component retention times to identify missidentifications

BP column

- n-Propylbenzene
- m-Ethyltoluene
- p-Ethyltoluene
- 1,3,5-Trimethylbenzene



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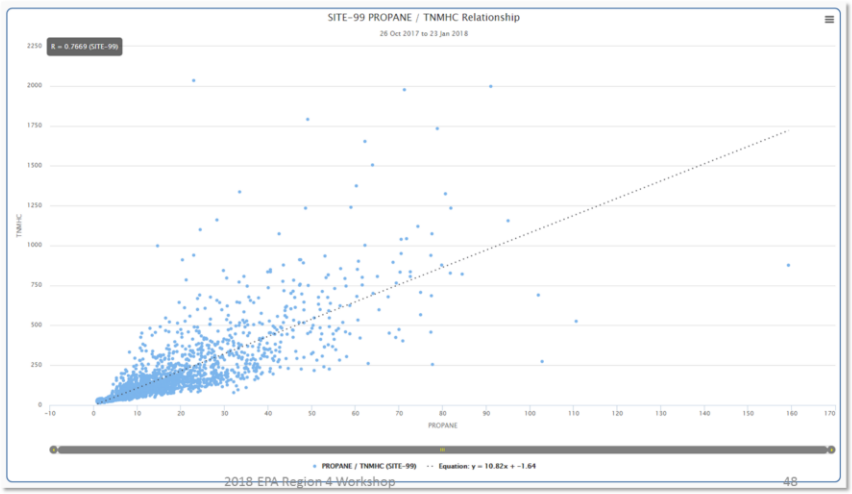
Here are retention time plots of 4 closely eluting targets on the boiling point column.

Ambient Scatter Plots

Scatter Plot of Propane and TNMHC to identify outliers



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MAX can also generate scatter plot relationships between targets.

Merlin AutoGC Xplorer

- Ingestion of ASCII Text files from PerkinElmer or Markes/Agilent PAMS VOC AutoGC Systems
  - Format specific native output files from Totalchrom or EZChrom data systems
  - Data loaded from zip files or individual hourly files
  - Re-loading of reprocessed data accepted and flagged as reprocessed
- Database capable of holding multiple years of data
  - Users are responsible for archiving original raw data
  - Graphing of large data sets
  - Automatic association with AQS parameter codes
  - User configured site parameters
    - Target list user defined
    - Quality control components, concentrations and pass/fail limits
    - Tracks Certificates of Analysis concentrations for each new quality control across years
- Cloud based secure server
  - User defined access levels for operators, validators and administrators
  - User defined site access

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MAX cloud services are designed to allow the uploading and review of data for validation prior to generation of AQS data sets.

- It requires a specific text output currently for PE or Agilent data
- It allows uploading using zipped files
- Allows reloaded data after reprocessing

It is an SQL database

- Capable of holding years of data
- Graphing large amount of data
- Automatic association with AQS parameter codes
- Allows user defined target lists and pass/fail
- Tracks C of A concentrations for recovery calculations

It is on a secure server

- Has user defined access levels for operators, validators and administratiors
- As well as user defined site access.

Merlin AutoGC Xplorer

Questions?

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Scrolling down on the QuickLook shows results from both chromatographic columns. Filenames link directly to the information from each ASCII text file which was ingested into the system.