STi | Sonoma Technology

Two Years of CAS Auto-GC PAMS Monitoring

Successes and Challenges in Software/Hardware Implementation, Monitoring, and Data QC

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Background

Our experience:

- Operated CAS auto-GCs for more than two years at multiple sites
  - Daily operation and maintenance
- Data analysis and validation of PAMS VOC data for three years
  - Software: AirVision, PeakViewer, and R

Created a consistent, reproducible method for real-time monitoring and data analysis for PAMS systems

CAS = Consolidated Analytical Systems

VOCs = Volatile organic compounds

Daily Data Assessment

- Hourly/Daily data alarms in AirVision
  - High and High-High alarms for individual parameters based on historical site analysis
  - Zero concentration alerts for abundant species
- Daily R Markdown Report
  - Summary of alarms and flags
  - Daily concentration box plots
  - Summary of rate of change alerts
  - Time series of parameter groups
  - Scatter plots of co-emitted species

Daily Data Assessment

PAMS daily report

2022-08-04

Daily Data Check:

```
## [1] "Expected substances missing from data: "
```

Flags

```
## [1] "No flagged observations"
```

NA Values

- The table below lists substances with 3+ missing observations on the report date, and the hours that the observations were missing.

substance	Count of missing observations	Hours

Alarms

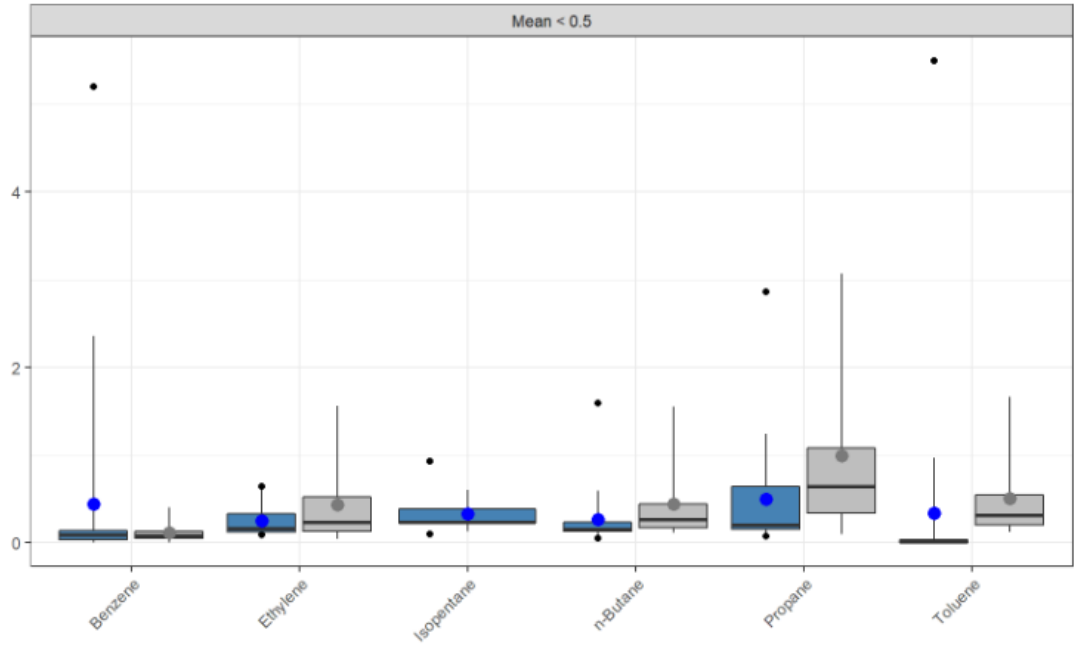
Required Parameters

```
## [1] "No Required Parameter alarms"
```

NMTHC and TNMOC

date	substance	value	flags	type	alarm_type
2022-08-04 05:00:00	TNMOC	9983.98		Optional/Other	High-high
2022-08-04 08:00:00	TNMOC	303.01		Optional/Other	High-high

Summary Statistics



Summary Stats Key Outliers

Values in the table below are:

- Both > 1 ppb **and** > 3*SD + mean of daily values for that substance

substance	date	mean	sd	value
2,2,4-Trimethylpentane	2022-08-04 11:00:00	0.19	0.57	2.62
Benzene	2022-08-04 11:00:00	0.44	1.20	5.20
Ethane	2022-08-04 00:00:00	0.89	0.39	2.22
n-Butane	2022-08-04 00:00:00	0.26	0.33	1.59
Propane	2022-08-04 00:00:00	0.50	0.65	2.86
TNMOC	2022-08-04 05:00:00	495.73	2175.00	9983.98
Toluene	2022-08-04 11:00:00	0.33	1.20	5.50

Daily Data Assessment

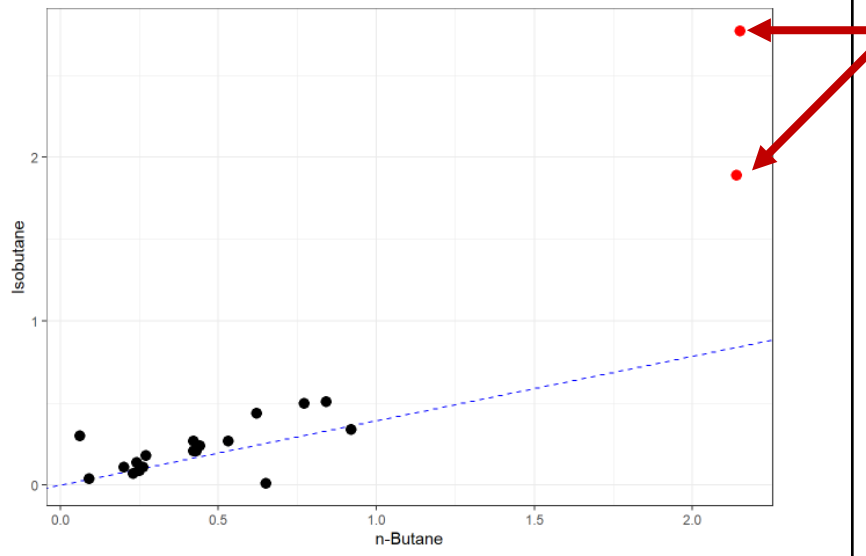
Rate of Change Alerts

Values will be flagged for rate-of-change if:

- The value increases or decreases by an order of magnitude >= 100 (e.g. New Value/Old Value > 100 or New Value / Old Value < 0.001)
- The value changes by 10 or greater from 0.00 (e.g. Old Value = 0.00, New Value = 12.00)

date	substance	value	next_value	flag
2022-08-04 08:00:00	Benzene	2.36	0.02	Value changed by order of magnitude >= 100
2022-08-04 11:00:00	Toluene	5.50	0.01	Value changed by order of magnitude >= 100

Ratio Plots



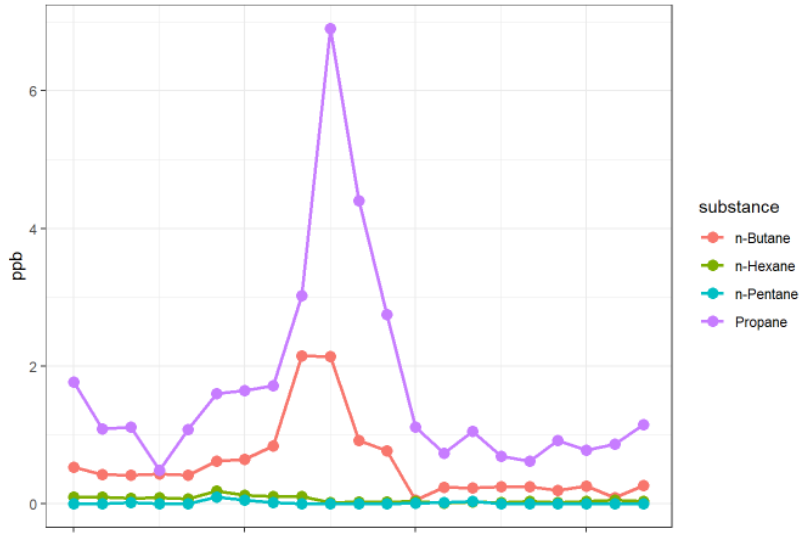
Suspect points are indicated

Check typical anthropogenic diurnal profiles

Diurnal Profiles

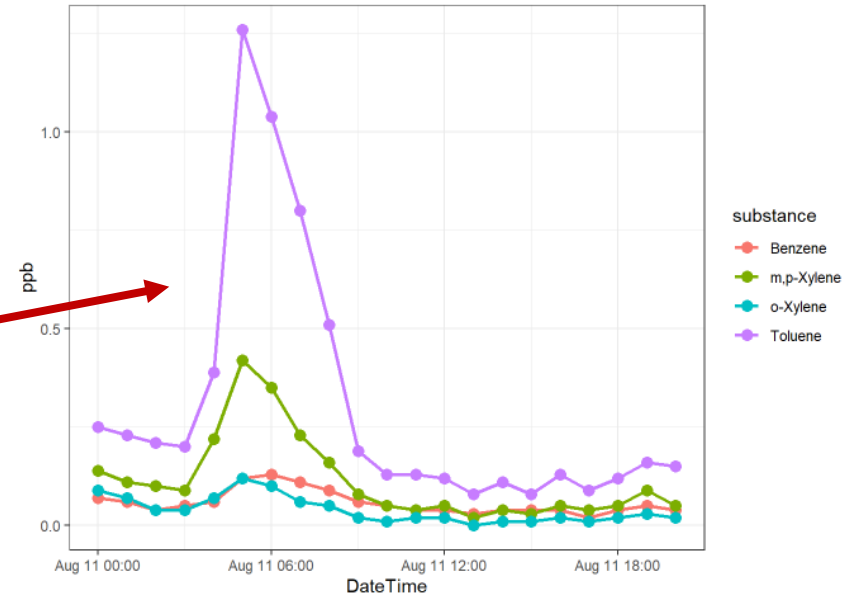
Alkanes

- Timeseries for Alkanes (Propane, n-Butane, n-Pentane and n-Hexane)



BTEX

- Timeseries for BTEX (Benzene, Toluene, m-Xylene, p-Xylene, o-Xylene)

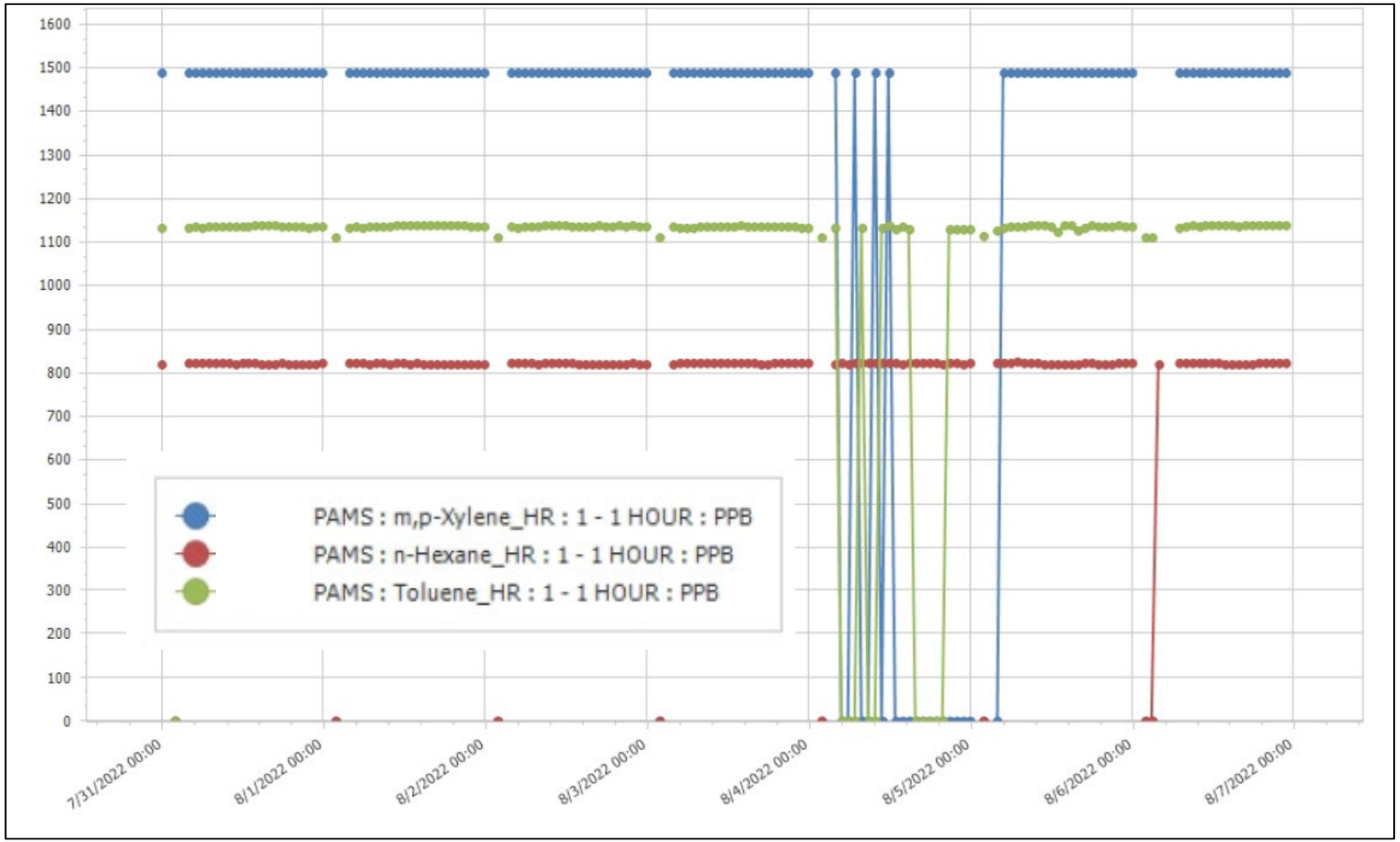


Weekly Data Assessment

- Automated Reports from AirVision
  - Six basic reports:
    - Time series of BTEX
    - Time series of Alkanes
    - Pollution rose of Benzene
    - Pollution rose of Propane
    - Time series of n-Hexane, Toluene, and m,p-Xylenes retention time
    - TNMOC/PAMSHC ratio
- Weekly R Markdown Report
  - All the same information as the daily reports
  - Added assessment of CAL, CYL, and ZERO behavior

Weekly Data Assessment – AirVision

Time Series of Retention Times

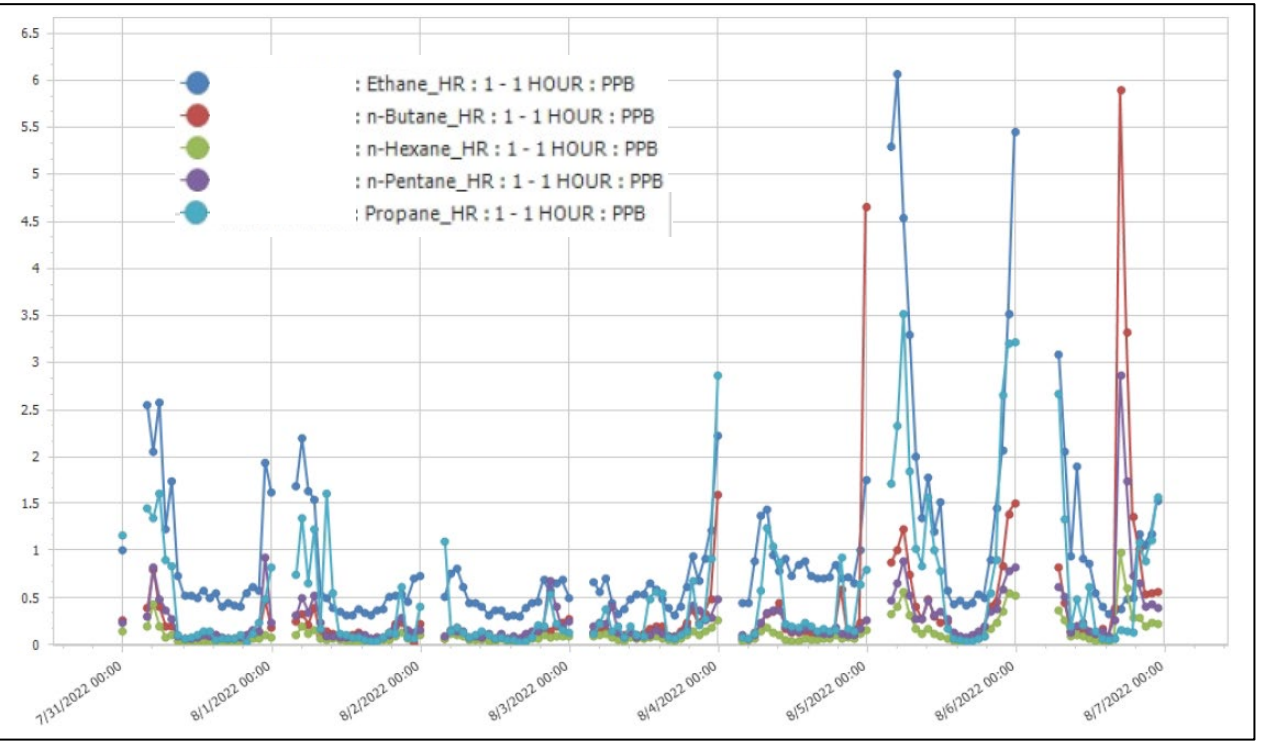


Inform the QC process:

- m,p: Xylenes most likely to show retention window shifts in C6-C12
- n-Hexane: an abundant parameter that could show retention window shift of C2-C6
- Monitor other troublesome species for retention shifts

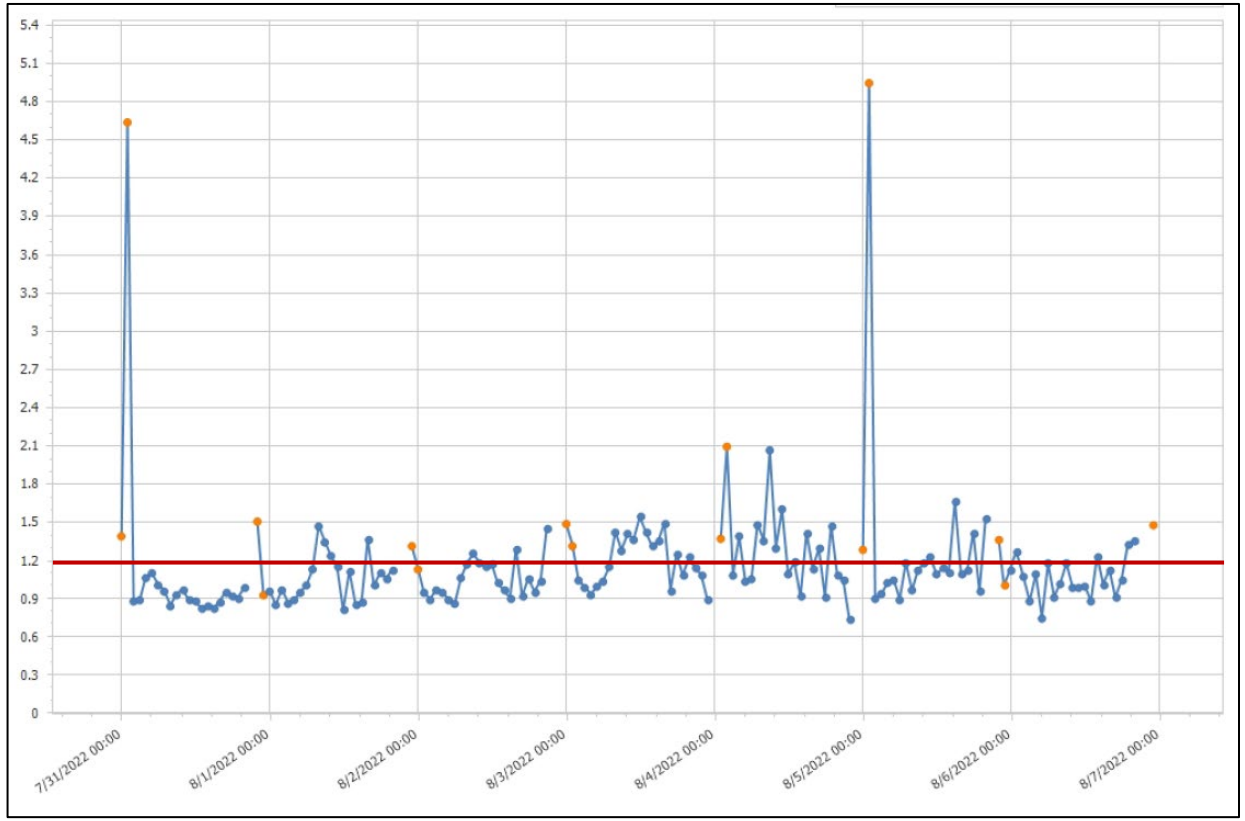
Weekly Data Assessment – AirVision

Alkane Time Series



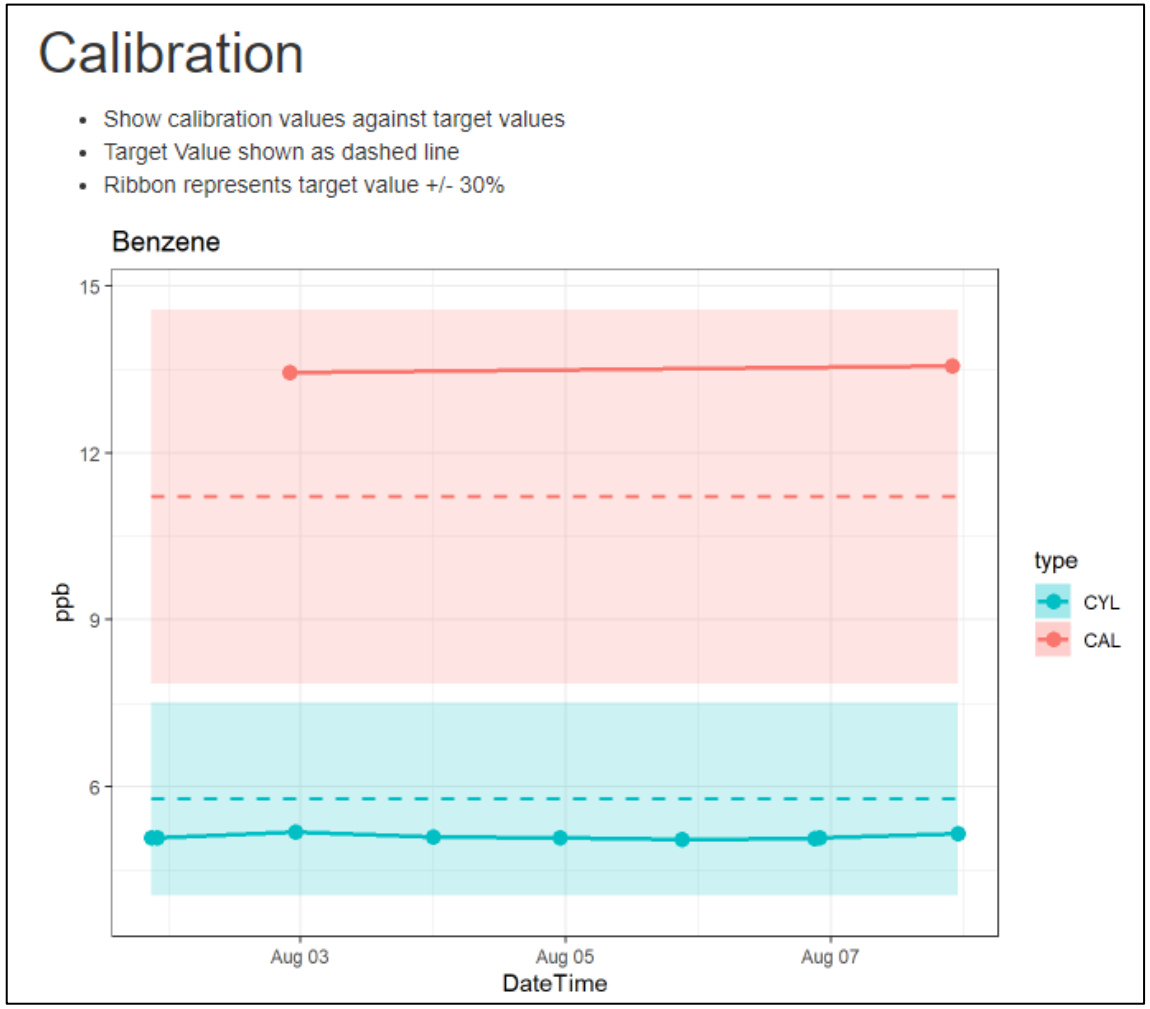
Check the diurnal profile and typical concentration of PAMS parameters

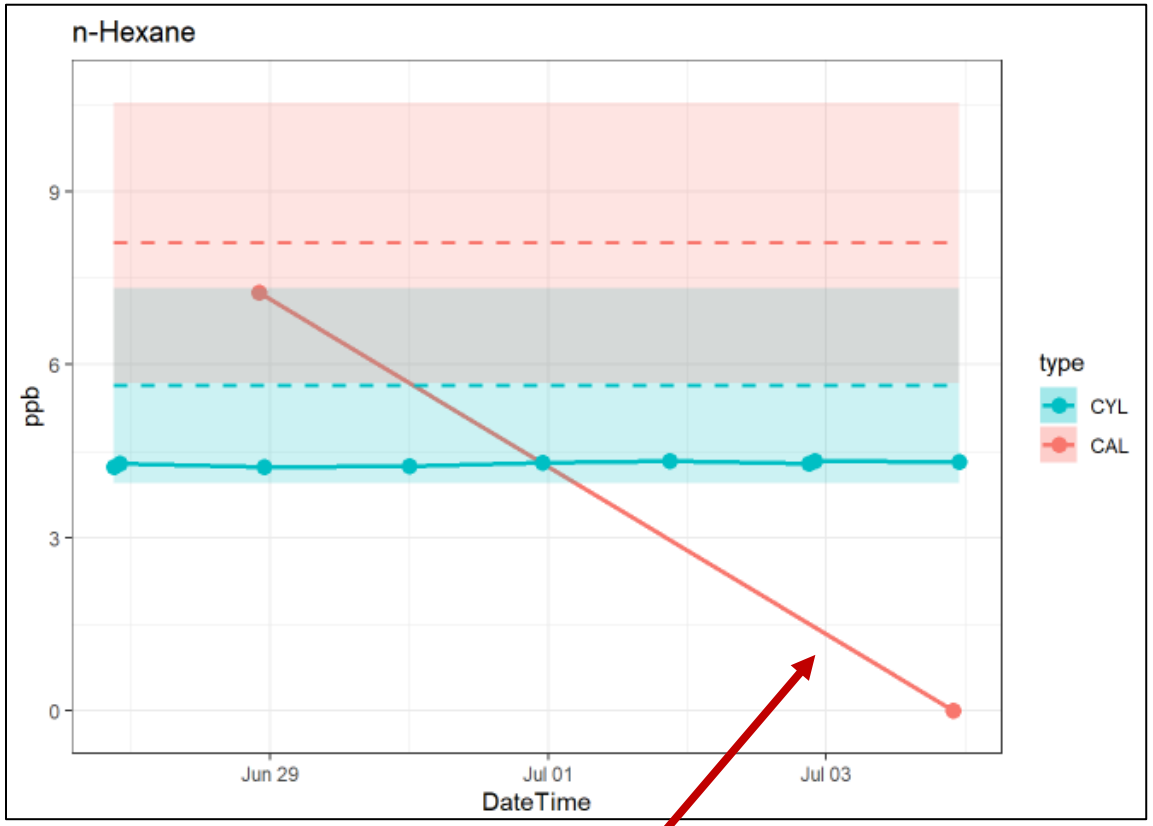
TNMOC/PAMSHC



Determine if concentrations of unknown VOCs are higher than expected

Weekly Data Assessment – R Report





Need to update substance table, possibly shifted out of retention window

Data Reprocessing and QC

- Visualization and data flagging occur in R and AirVision
- CAS Auto-GC data reprocessing occurs in PeakViewer

  Basic processes:

  1. Review CAL → CYL → ZERO → AMB
  2. Visualize 5-7 days of AMB data at a time
  3. Find the predominate pattern in chromatograms

     This could mean (a) noting all atypical chromatograms and removing them from the current reprocessing pool, (b) finding the date and time of a major retention window shift, and/or (c) determining typical shifts in the chromatogram baseline
  4. Create the minimum number of substance tables needed to reprocess data
  5. Establish integration parameter updates
  6. Reprocess AMB data in chunks based on typical patterns

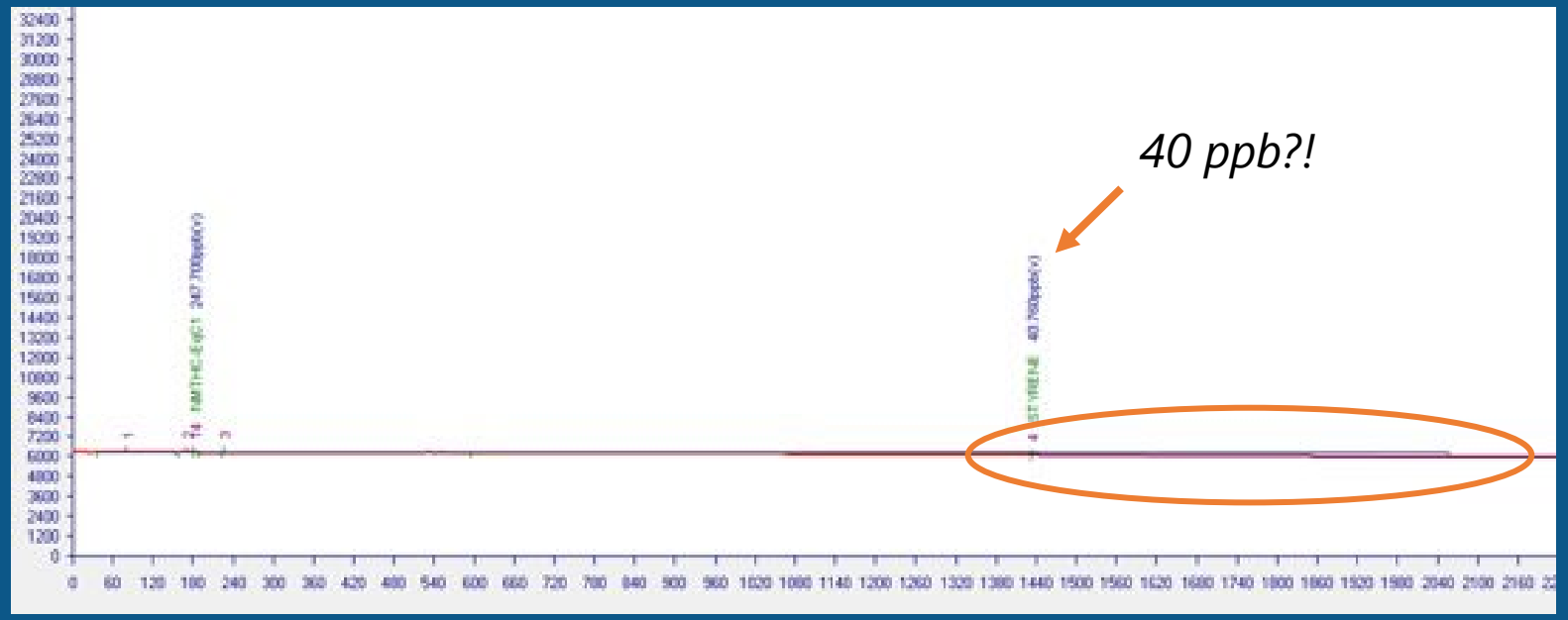
We do NOT use manual integration options in PeakViewer since it is not reproducible

Typical Reprocessing Issue #1

Peak tailing anomalously long

<u>Problem:</u>

Concentration is too large because of peak tailing



Solution:

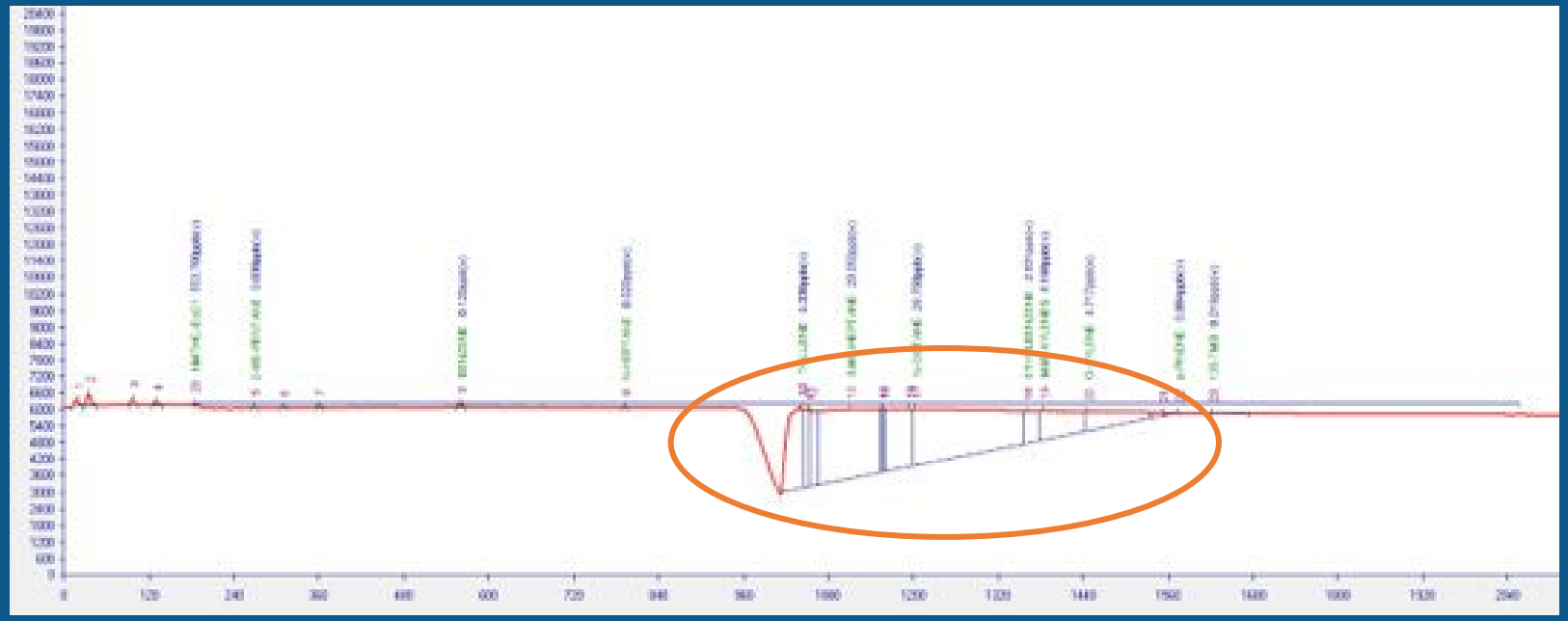
Typically, increasing the slope integration parameter for the entire width of the peak will resolve this.

Typical Reprocessing Issue #2

Detector malfunction mid-chromatogram

<u>Problem:</u>

Parameters after the malfunction are incorrectly integrated



Solution:

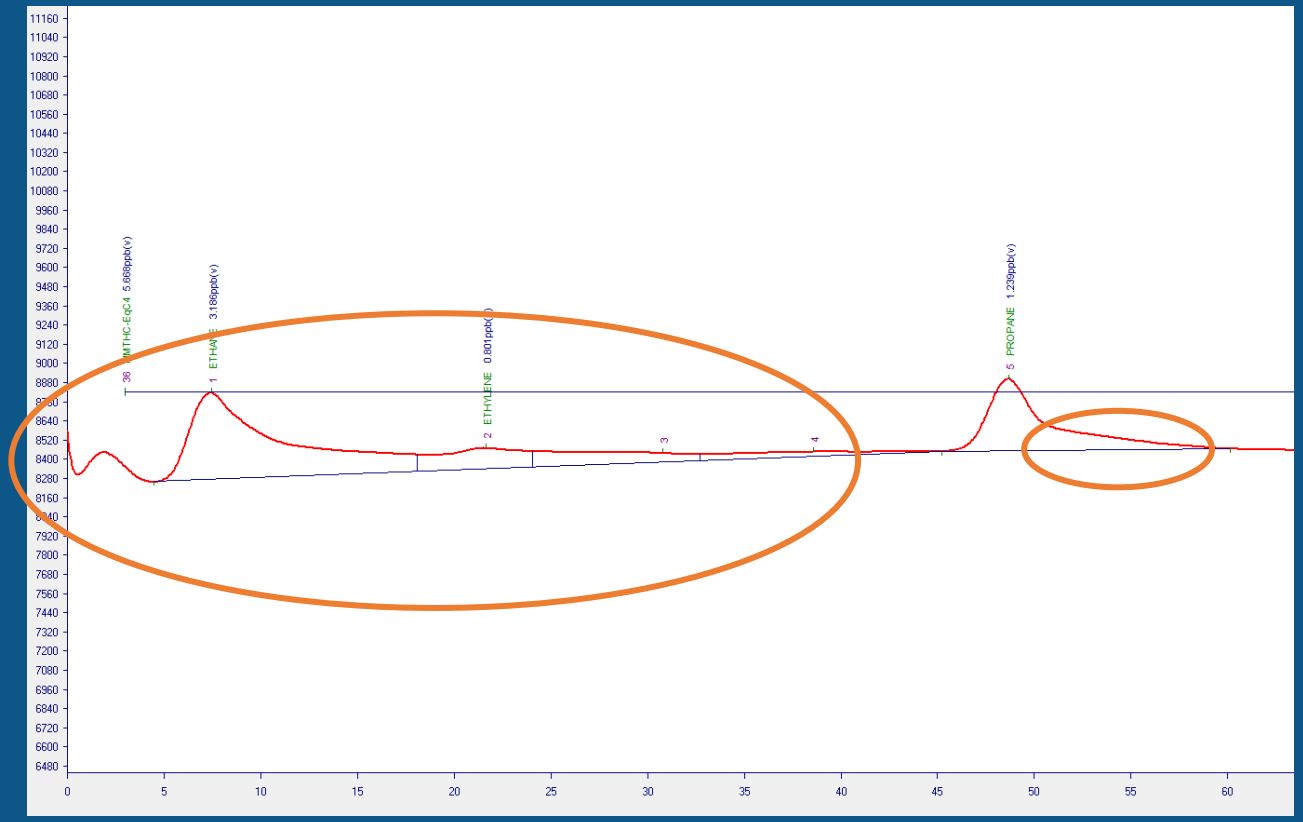
For a short period after the detector malfunction (~50 seconds), increase the drift to a very large value (we've used up to 2000). Invalidate TNMOC.

Typical Reprocessing Issue #3

Peak tailing and incorrect integration at the beginning of C2-C6

<u>Problem:</u>

Concentrations are too large



Solution:

Make multiple integration parameter updates for Ethane, Ethene, and Propane. Increase slope and drift for each to compensate for the unstable baseline at the beginning of the chromatogram

Typical Reprocessing Issue #3

Peak tailing and incorrect integration at the beginning of C2-C6

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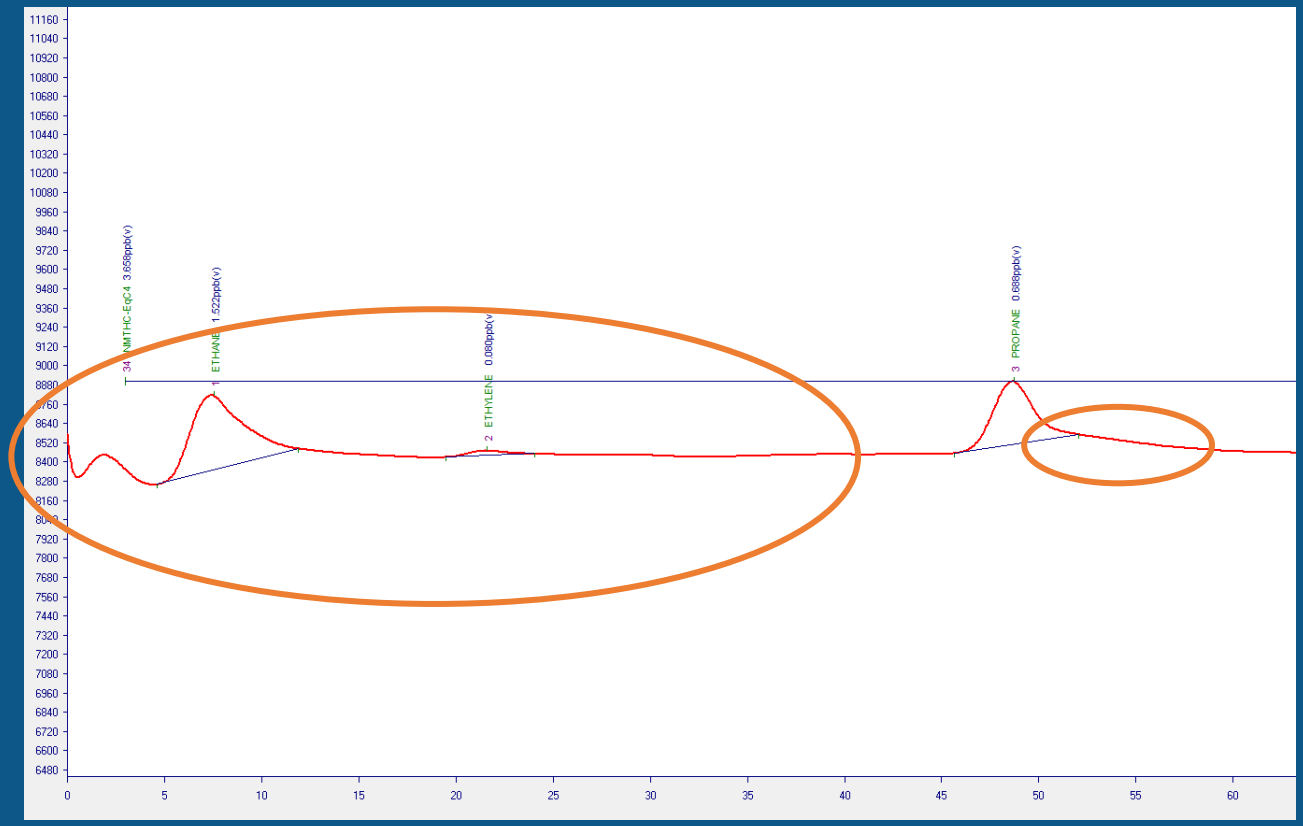
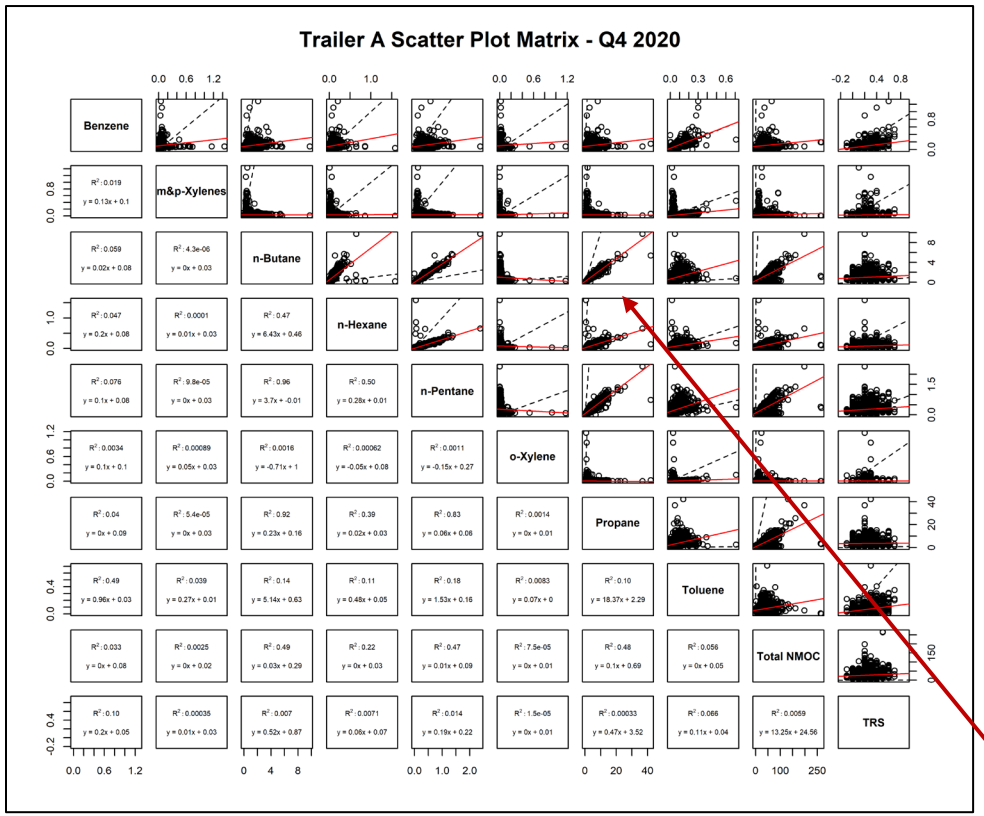


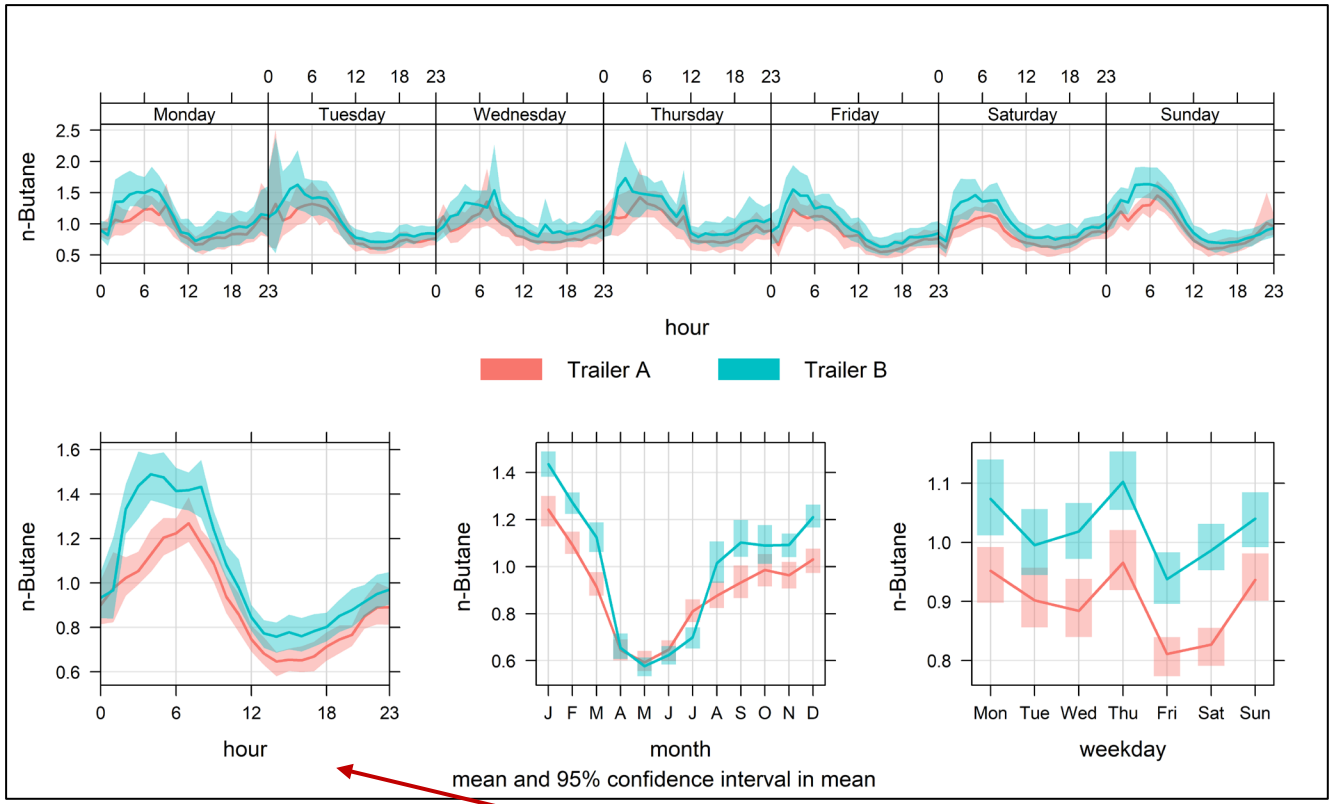
Solution:

Make multiple integration parameter updates for Ethane, Ethene, and Propane. Increase slope and drift for each to compensate for the unstable baseline at the beginning of the chromatogram.

Visualize – Again!

After reprocessing, review data again via time series, scatter plots, etc.





Check co-emitted species

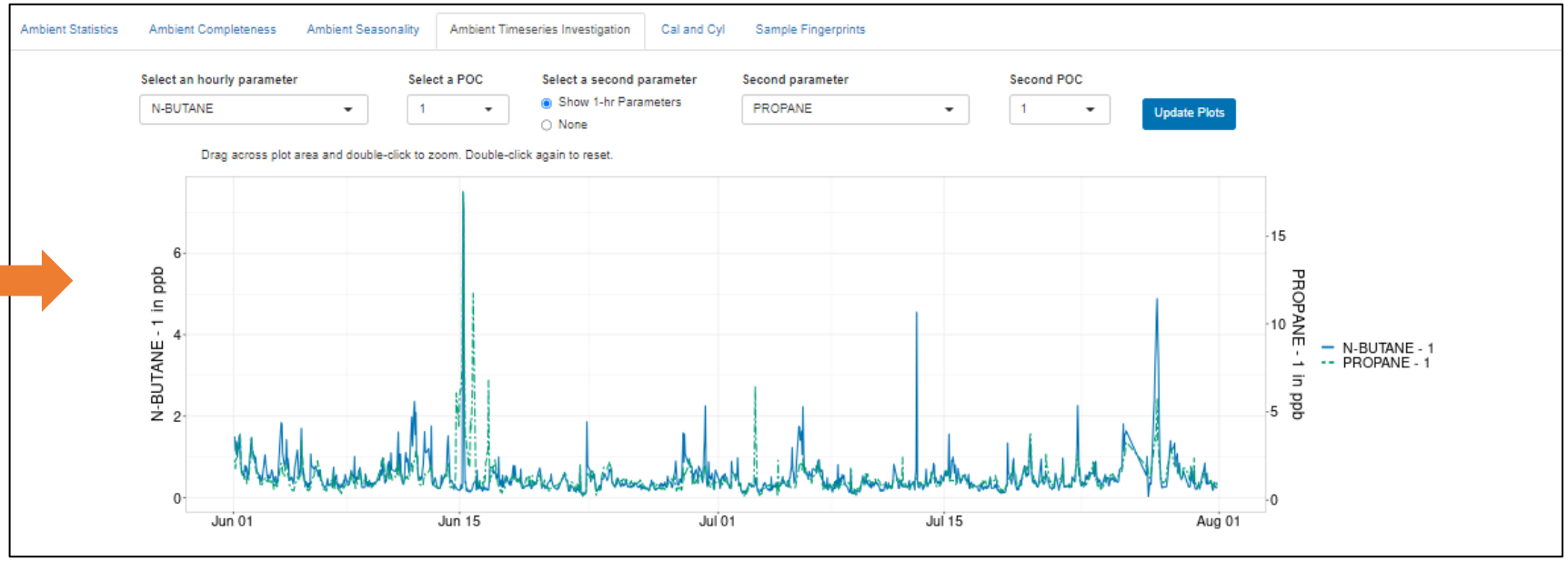
Check diurnal profiles

Summary

We've developed a reproducible, consistent PAMS real-time data monitoring plan and data reprocessing/analysis procedure.

- Daily/weekly data checks and alerts
- Consistent procedure for chromatogram reprocessing and review with data visualization

We also interactively visualize our PAMS data using data dashboards



Presenters

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Questions?

Visit with us about PAMS monitoring & QC at the Sonoma Technology booth!

Come explore the **PAMS Dashboard** *and check out the suite of dashboards available:*

- *Near-Road Dashboard*
- *NCore Dashboard*
- *FRM-FEM Comparability Dashboard*
- *Ozone, CO, NO, NO_2, NO_y, SO_2, and FRM Dashboards*

Extra Slides

Acronyms

- AMB = ambient sample chromatogram
- Auto-GC = automatic gas chromatograph
- BTEX = combination of combustion VOC: benzene, toluene, ethylbenzene, o-xylene, and m,p-xylenes
- CAL = internal calibration chromatogram
- CAS = Consolidated Analytical Systems
- CYL = external (cylinder) calibration chromatogram
- C2-C6 = CAS GC that analyzes samples for VOCs between two and six carbons
- C6-C12 = CAS GC that analyzes samples for VOCs between two and twelve carbons
- PAMS = Photochemical Assessment Monitoring Station
- PAMSHC = PAMS hydrocarbons (does not include unknown VOCs)
- ppb = parts per billion
- QC = quality control
- R = free statistical and data science software
- TNMOC = Total Non-Methane Organic Carbon (includes unknown VOCs)
- VOC = Volatile Organic Compound
- ZERO = blank chromatogram

Sample Dashboard

Create quick reports

VOC Concentrations:
ppbv ppbC

Generate PDF report | Download RData

Data exploration types

Time Series | Compare Concentrations | 3D Scatter | Elution Chart | Box Plots | Summary Data Table

Show Table?

Select Location: Site A

Select Parameter: 2-Methyl-1,3-butadiene (Isoprene)

Download Parameter-Site Data | Download All Site Data

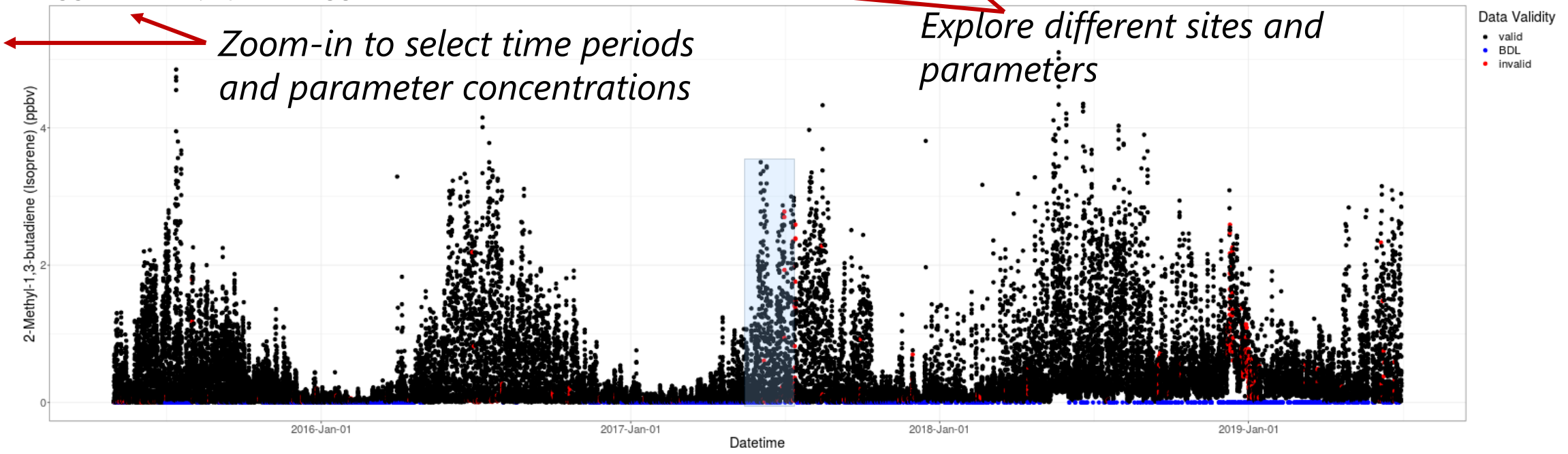
Set Concentration Max
Ex: 25.2

Set Concentration Min
Ex: 0.2

Zoom-in to select time periods and parameter concentrations

Explore different sites and parameters

Highlight Data to Show in Table (below) - Double-Click in Highlighted Area to Zoom



Set Start Date
Ex: 2015-11-01

Set End Date
Ex: 2016-01-01

Reset Data | Show All | Search:

Set Validity | Invalidate All - Outlier | Invalidate All - Baseline | Invalidate All - Other | Finalize Data

Date & Time	Parameter	Concentration (ppbv)	Validity	Change Validity
2017-05-15 02:00	2-Methyl-1,3-butadiene (Isoprene)	0	BDL	valid
2017-05-15 03:00	2-Methyl-1,3-butadiene (Isoprene)	0	BDL	valid
2017-05-15 04:00	2-Methyl-1,3-butadiene (Isoprene)	0	BDL	valid

Set validity manually