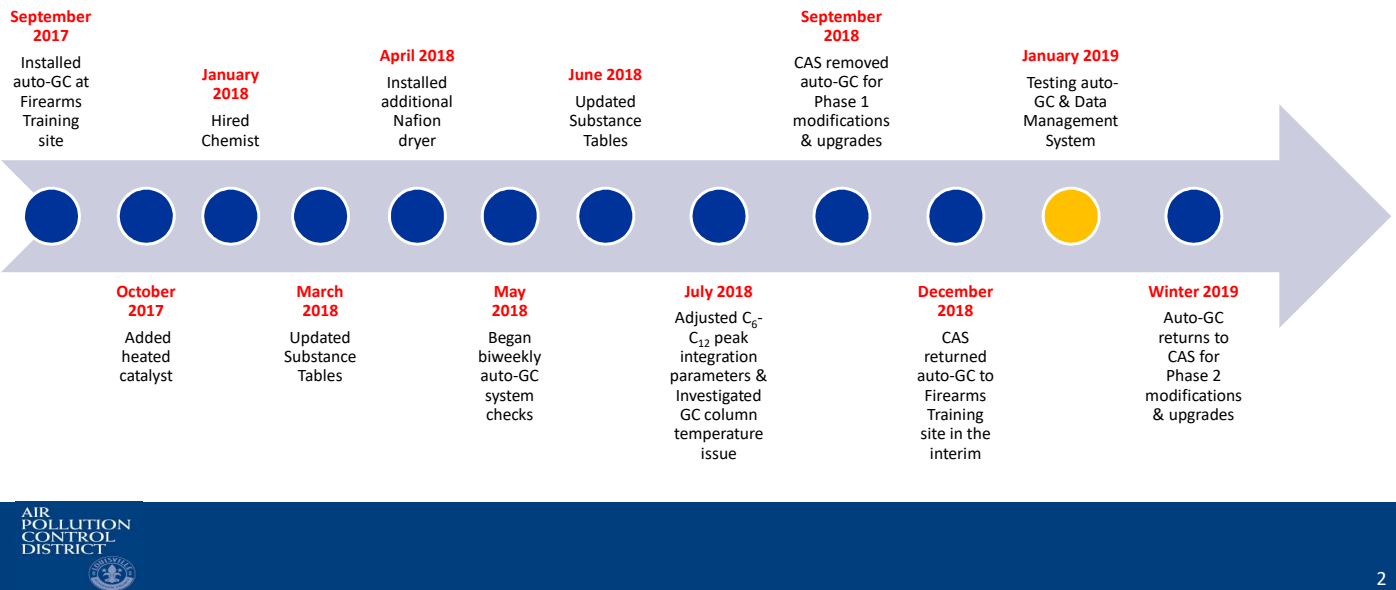


# APCD Air Toxics Update

Air Pollution Control District  
January 16, 2019



# Air Toxics Auto-GC Timeline



- Firearms Training site is downwind of Rubbertown facilities
- Heated catalyst installed to remove VOC contaminants in zero air
- Substance Tables are auto-GC lookup tables containing VOCs of interest & their retention time windows (minimum & maximum time one expects VOC to be detected after traveling through the column)
- Substance Tables updated after testing canisters containing multiple VOCs
- Nafion dryer to remove water vapor from samples, hydrogen gas. Humidity shifts retention times on C3-C6 GC (analyzes lighter VOCs)
- Biweekly system checks of temperatures, pressures, etc. to ensure system is running properly
- Adjusting peak integration parameters improved sensitivity of C6-C12 GC by allowing peaks with smaller peak areas to be integrated
- Auto-GC removed for Phase 1 modifications & upgrades to address humidity issues, column temperature issues, & coelution issues
- While waiting for more parts from the manufacturer, CAS (auto-GC vendor) returned system (per APCD's request) to Firearms training to allow data collection to continue & to test the Data Management System update for handling auto-GC VOC data
- Phase 2 modifications & upgrades pending

# CAS Phase 1 Modifications/Upgrades Complete

Modification/Upgrade	Purpose
Added cylinder port	Connect 2 cylinders to auto-GC system
Nafion dryers under vacuum	Improve peak retention time stability
Single high vacuum pump	Improve sample residence time
Added dryers & purifiers	Dry and clean support gases
New internal sample tubing	Provide a cleaner system
Added fans to each GC	Improve GC column temperature control
Replaced pressure control valves	Improve GC column head pressure control
Replaced various other components	Annual maintenance

- Additional cylinder port gives option for additional calibration testing
- Residence time = time a collected ambient sample is in the sample probe (from inlet to auto-GC). High vacuum pump decreases residence time, single pump (instead of 2) provides uniform flow to each GC.
- Support gases include zero air & hydrogen gas
- Added fans should help cool GC column oven faster
- New pressure control valves are not affected by temperature

# CAS Phase 2 Modifications/Upgrades Pending

- Once CAS receives parts from manufacturer

Modification	Purpose
Longer C <sub>6</sub> -C <sub>12</sub> GC column	Improve peak separation
Update GC cycle to 60 minutes	Improve peak separation & make consistent with PAMS program
Mass flow controllers	Improve sample flow control
3-phase trap & Peltier cooler	Capture more volatile VOCs (propane, propene, ethane, ethene)
Rebuild GC ovens	Improve temperature control
Replace various components	Annual maintenance

- Pending the vendor receiving parts from manufacturer, these modifications & upgrades will be completed in Winter 2019
- Longer column should help reduce coelution of VOCs, which is an issue on C6-C12 GC

# Quality Assurance / Quality Control

Complete	Ongoing	Pending
Draft Quality Assurance Project Plan (QAPP)	Biweekly auto-GC system checks	Cylinder with 69 VOCs (PAMS & toxic compounds)
Draft QAPP submitted to EPA October 2018	Examine chromatograms daily	Calibrate GCs with internal standards
		Run nightly checks with cylinder
		PAMS VOC canister subscription service

# Preliminary APCD Data Quality Score (DQS)

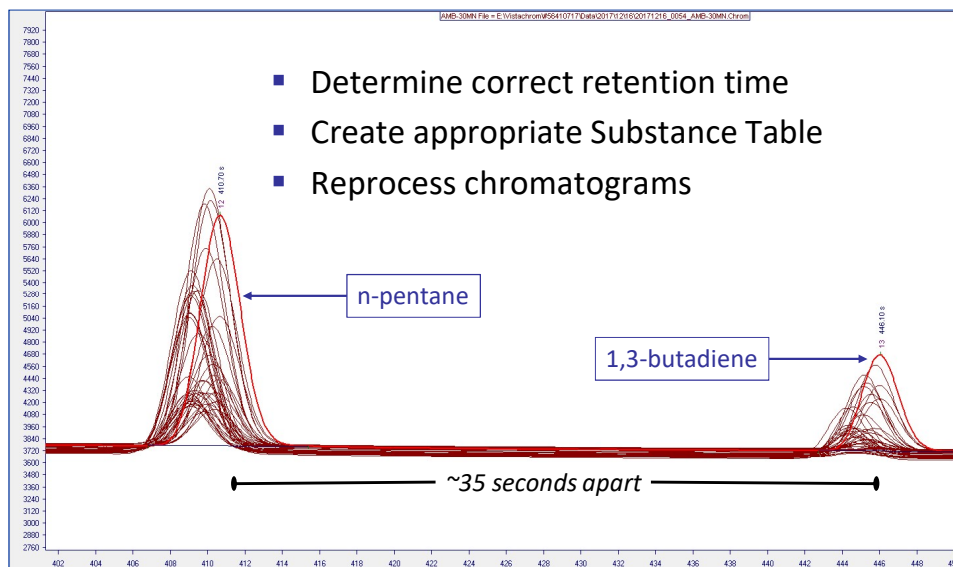
- Current method to communicate confidence in VOC peak identification

Retention Time Shifting Score	Coelution Score	DQS
S – Satisfactory Low chance RT shifting > RTW Post-processing not likely required	5 – no known coelution	Green – low RT shifting potential, no significant coelution concerns
U – Unsatisfactory High chance RT shifting > RTW Post-processing likely required	4 – partial coelution, each peak quantified	Yellow – high RT shifting potential OR coelution concerns
	3 – partial coelution, quantification is concentration dependent	Red – high RT shifting potential AND coelution concerns
	2 – complete coelution with VOC of interest, report as sum or use other GC to verify	
	1 – complete coelution with unidentified VOC	

- RT = retention time, how we identify VOCs present in a sample
- RTW = retention time window, minimum to maximum RTs we expect to “see” a particular VOC
- RT shifting due to improperly dried sample, water vapor not removed before sample enters separation column causing RT to be inconsistent each run
- Coelution = 2 or more compounds exit column at same time therefore detected at the same time, difficult to quantify each compound

## Steps to Post-Process Data

Ambient  
VOC Data  
12/16/2017



- Determine correct retention time
- Create appropriate Substance Table
- Reprocess chromatograms

- This is an example of the steps taken to post-process chromatograms for 1,3-butadiene
- Since n-butane occurs in nearly all ambient chromatograms, use it as a reference peak to determine 1,3-butadiene peak (should elute about 35 seconds after n-butane)
- Once 1,3-butadiene peak located, create Substance Table with appropriate RTW
- Reprocess chromatograms with correct RTW to identify & quantify 1,3-butadiene

# APCD Target Compound Summary

	STAR TAC Category	APCD Target Compound	RT Shifting Score (S/U)	Coelution Score (5-1)	Raw DQS	Post-processed DQS
C <sub>3</sub> -C <sub>6</sub> GC	1	vinyl chloride	U	3	Red	Yellow
	1	*1,3-butadiene		5	Yellow	Green
	1	methylene chloride		TBD	TBD	TBD
C <sub>6</sub> -C <sub>12</sub> GC	1	acrylonitrile	S	1	Yellow	Yellow
	1	chloroform		1	Yellow	Yellow
	1	*benzene		3	Yellow	Yellow
	1	*carbon tetrachloride		3	Yellow	Yellow
	4	ethyl acrylate		3	Yellow	Yellow
	1	trichloroethylene		1	Yellow	Yellow
	4	methyl methacrylate		3	Yellow	Yellow
	4	methyl isobutyl ketone		2	Yellow	Yellow
	2	*toluene		5	Green	Green
	1	*tetrachloroethylene		2	Yellow	Yellow
	4	*ethylbenzene		3	Yellow	Yellow
	1	bromoform		2	Yellow	Yellow
	4	*styrene		4	Green	Green
	1	1,4-dichlorobenzene		3	Yellow	Yellow

## Data Quality Score (DQS)

**Green** – low RT shifting potential, no significant coelution concerns

**Yellow** – high RT shifting potential OR coelution concerns

**Red** – high RT shifting potential AND coelution concerns

\*PAMS compound



Scores reflect current status and are subject to change following auto-GC modifications.

- This is a snapshot of APCD's current Data Quality Scores for 17 target compounds
- Goal is to have more "Green" raw DQSs after Phase 2 modifications & upgrades as well as addition of 69 component cylinder
- 1,3-butadiene is a compound we have more confidence in



# 1,3-Butadiene Summary

Month / Year	Average (ppbv)	Minimum (ppbv)	Maximum (ppbv)	Median (ppbv)	Data Completeness (%)
November 2017	0.16	< 0.05	5.96	< 0.05	91
December 2017	0.13	< 0.05	6.60	< 0.05	94
January 2018	0.14	< 0.05	24.37	< 0.05	91
February 2018	1.99*	< 0.05	329.96	< 0.05	90
March 2018	0.07	< 0.05	9.28	< 0.05	90
April 2018	0.08	< 0.05	7.23	< 0.05	85
May 2018	0.46*	< 0.05	95.61	< 0.05	86
June 2018	0.39	< 0.05	77.32	< 0.05	76
July 2018	0.09	< 0.05	8.79	< 0.05	56
August 2018	0.47	< 0.05	18.79	0.06	88
September 2018	0.25	< 0.05	14.42	< 0.05	81

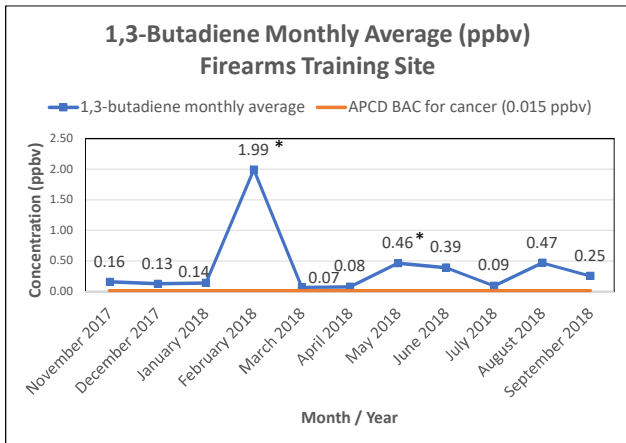
\*Monthly averages excluding localized events with winds from North are 0.17 ppbv (February 2018) & 0.35 ppbv (May 2018). Emissions from these events are under investigation.



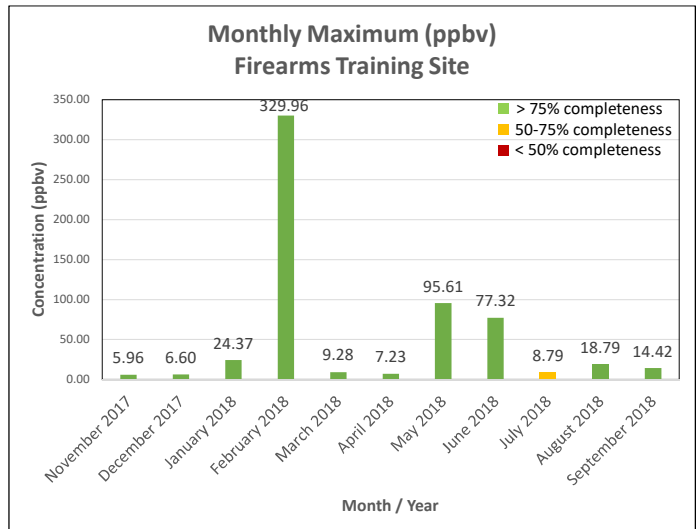
*Data are preliminary, have not been quality assured, and are subject to change.  
Current limit of quantification = 0.05 ppbv*

- Low data completeness from July 2018 due to C3-C6 flame ionization detector (FID) ignitor going out. Lost 2 weeks of data while waiting for part, replacing, and getting GC back online

# 1,3-Butadiene Summary



\*Monthly averages excluding localized events with winds from North are 0.17 ppbv (February 2018) & 0.35 ppbv (May 2018). Emissions from these events are under investigation.



Data are preliminary, have not been quality assured, and are subject to change.  
Current limit of quantification = 0.05 ppbv

- Graph on the left shows the monthly average values provided in Slide 9
- Graph on the right shows the monthly maximum values provided in Slide 9

# Questions?

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