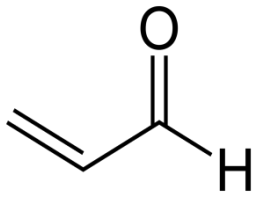
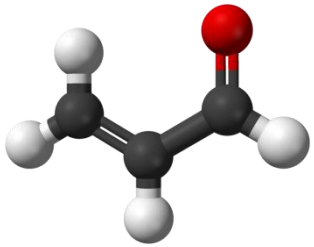


Acrolein



David Shelow, Joann Rice, Mike Jones, Julie Swift (ERG)

Office of Air and Radiation
Office of Air Quality Planning and Standards

Acrolein Measurement Methods

- TO11A: DNPH Cartridges
  - 2,4-dinitrophenylhydrazine (DNPH) coated silica gel
  - Pull air thru cartridge with pump
  - Extracted and analyzed by HPLC (UV)

- TO-15:
  - Sampling: Canister based
    - Subambient or pressurized
  - Analytical: Preconcentration/GC/MSD (SIM or SCAN mode)

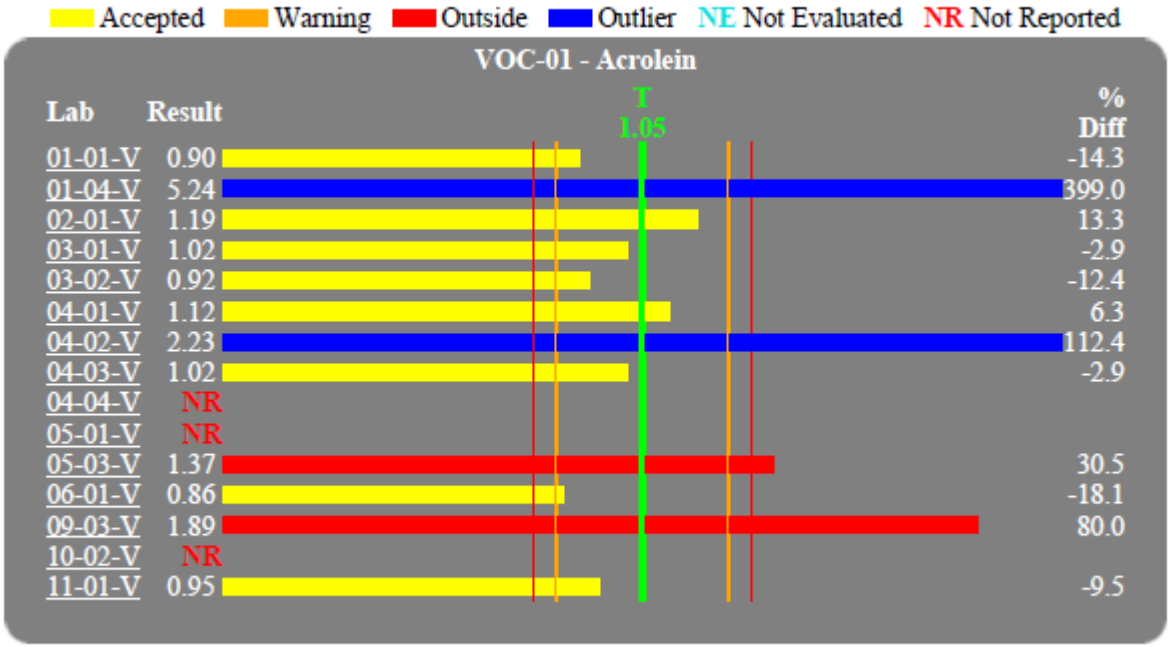
National Air Toxics Summary

Year	Mean		Max		#Obs	
	Canister	DNPH	Canister	DNPH	Canister	DNPH
2006	0.86	0.07	18.24	1.57	3200	1966
2007	0.72	0.15	16.43	12.16	5574	1823
2008	0.71	0.09	20.27	2.47	6281	1114
2009	0.80	0.03	23.63	0.28	1752	119

All Years	**0.77ug/m3**	**0.08**ug/m3

NATTS PT for Acrolein 2010

Study Number: 201001-V



NATTS PT for Acrolein 2010

Study Number: 201001-V

Accepted | Warning | Outside | Outlier | NE Not Evaluated | NR Not Reported

VOC-01 - Volatile Organics

Analyte	Avg	T	% Diff
Benzene	0.85	0.91	-6.3
1,3-Butadiene	0.96	0.82	16.9
Carbon tetrachloride	1.03	0.98	4.7
Chloroform	0.86	0.97	-11.2
1,2-Dibromoethane	1.06	1.00	6.3
1,2-Dichloropropane	0.95	0.99	-4.1
1,2-Dichloroethane	1.01	1.06	-4.7
Dichloromethane	1.03	1.11	-7.6
1,1,2,2-Tetrachloroethane	1.09	1.05	3.9
Tetrachloroethylene (PERC)	0.86	0.93	-7.9
Trichloroethylene	1.02	1.09	-6.0
Vinyl chloride	0.83	0.85	-1.8
cis-1,3-Dichloropropene	0.89	0.88	1.1
trans-1,3-Dichloropropene	0.94	0.89	5.8
Acrolein	1.56	1.05	48.5

Canister Method Concerns

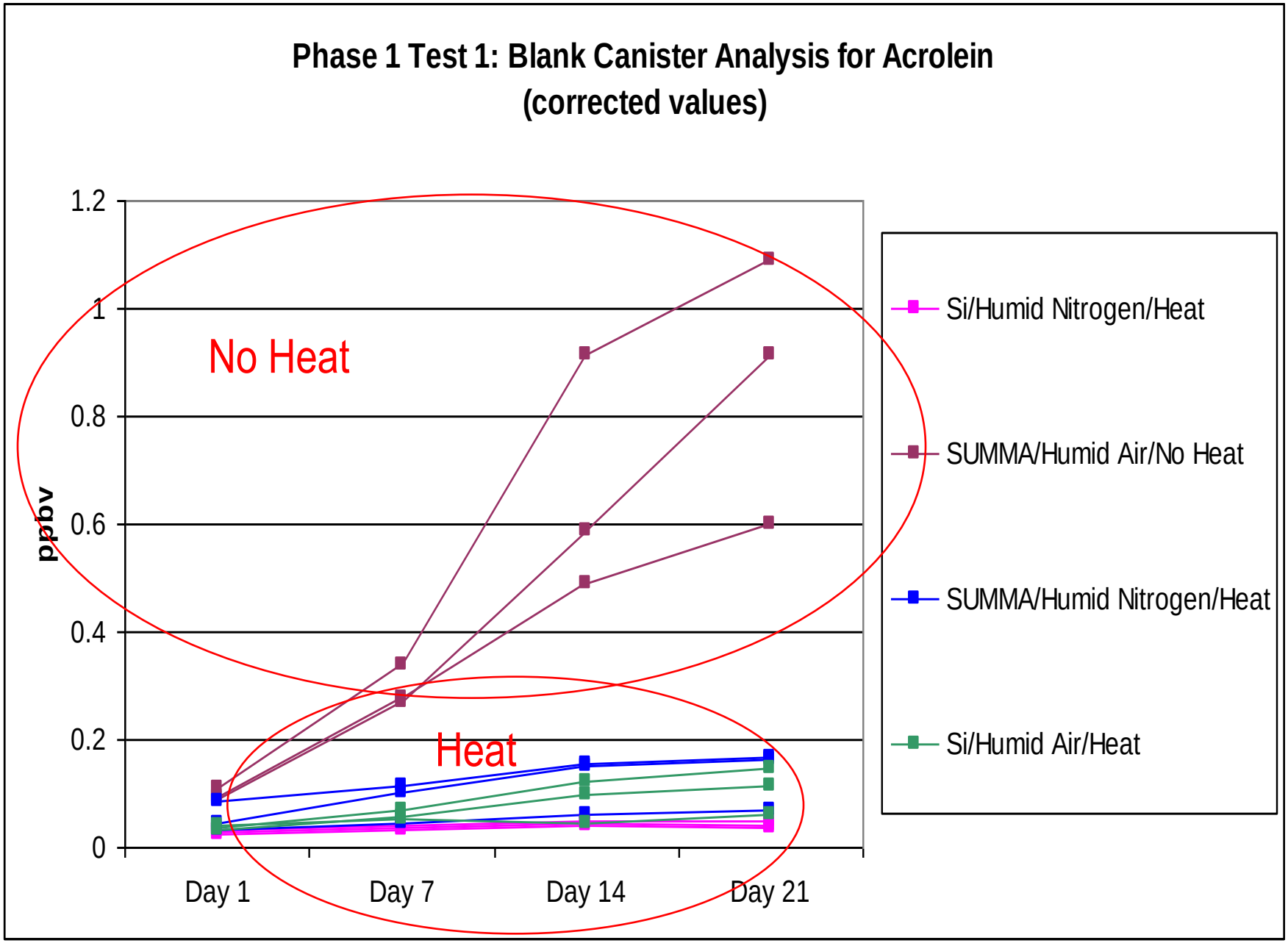
- School Air Toxics project
- Several State agencies expressed concern with Acrolein results
- NACAA Steering Committee members expressed concern about previous work showing growth of Acrolein in canisters

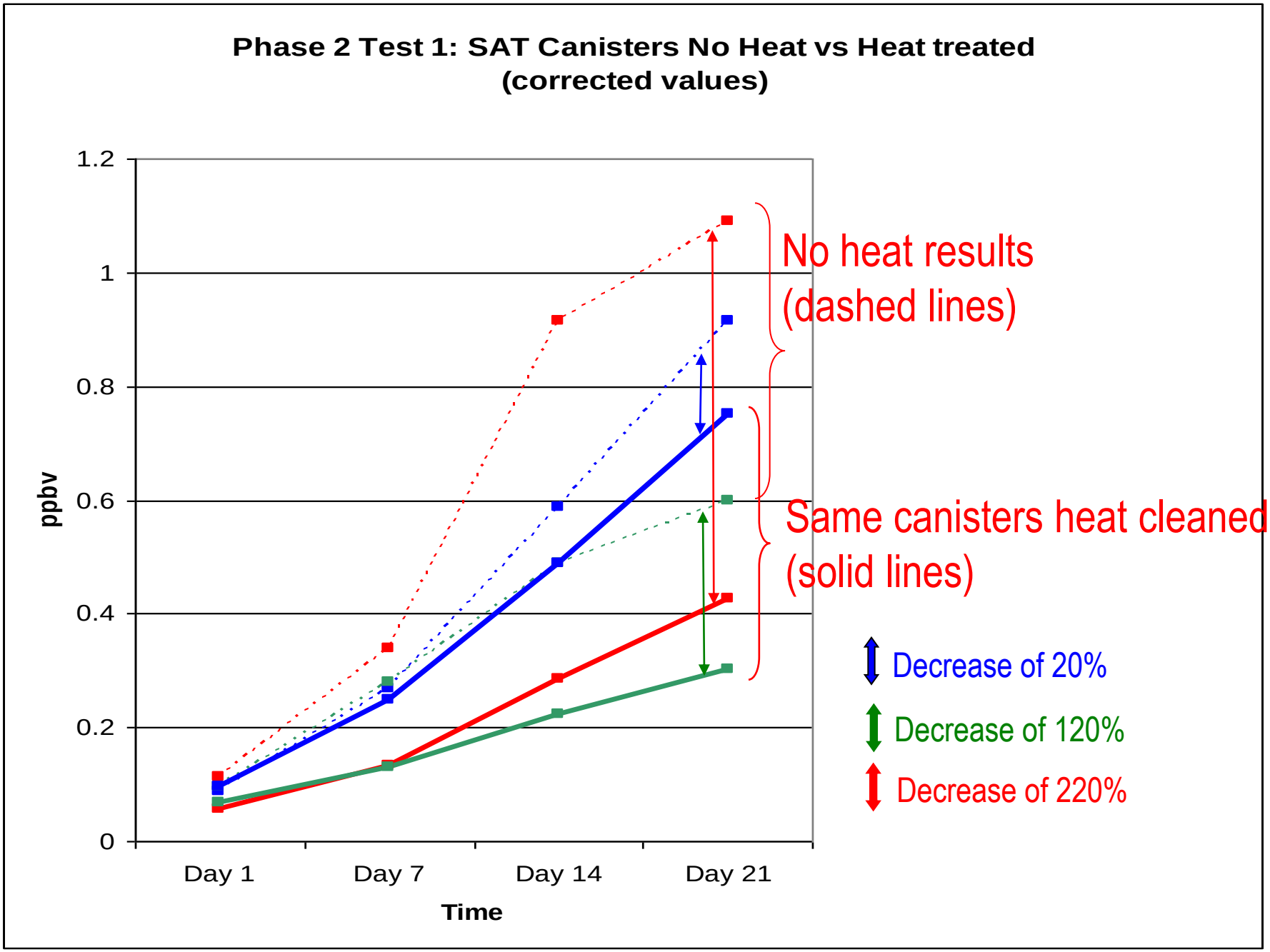
SAT DATA COMPARISON TO AQS

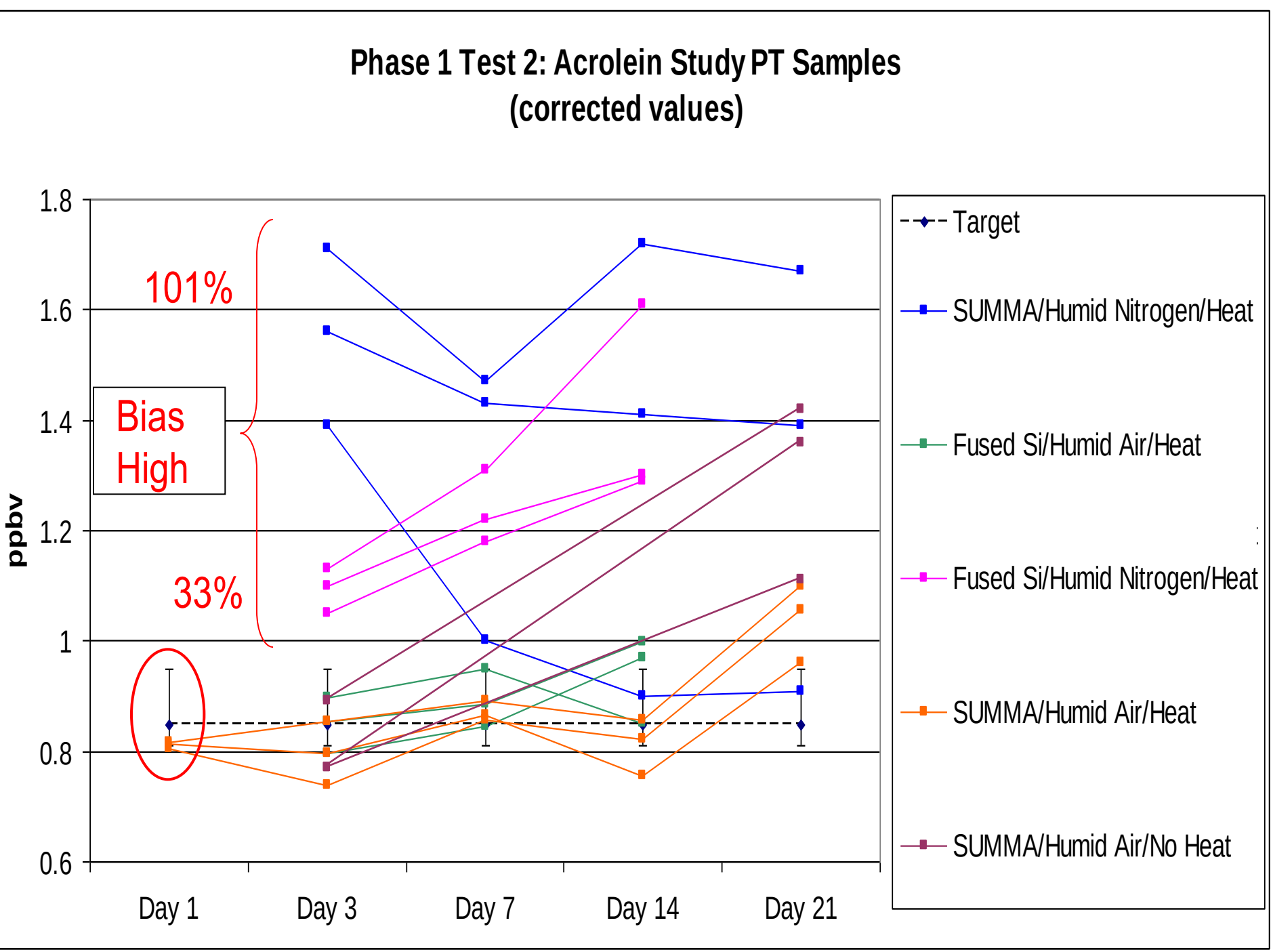
Site Code	State	Location Setting	Max ug/m3	Min ug/m3	Mean SAT values ug/m3	Mean State AQS value thru July - Dec, Location type
ALIN SCH	Indiana	URBAN	4.26	0.72	2.04	1.56
COWA SCH	Washington	URBAN	4.59	0.40	1.88	0.46
ESOH SCH	Ohio	RURAL	3.19	0.69	1.48	n/a
	Mississippi	RURAL	7.29	0.91	3.96	0.95
EHMS SCH	Mississippi	RURAL	4.98	0.58	2.86	0.95
FECA SCH	California	URBAN	4.31	1.10	2.81	1.33
LHID SCH	Idaho	RURAL	2.61	0.37	1.46	n/a
LEAL SCH	Alabama	URBAN	3.00	0.80	1.70	0.4
LSOH SCH	Ohio	SUBURBAN	4.86	0.47	1.91	n/a
LEIN SCH	Indiana	SUBURBAN	6.76	0.52	2.18	1.47
NEAL SCH	Alabama	SUBURBAN	4.26	0.30	2.21	0.4
SAPA SCH	Pennsylvania	SUBURBAN	2.68	0.38	1.34	0.45
SHWA SCH	Washington	SUBURBAN	2.10	0.52	0.99	0.38
SECO SCH	Colorado	RURAL	2.82	0.63	1.93	0.84
TEAL SCH	Alabama	SUBURBAN	4.04	0.67	1.89	0.4
TEOR SCH	Oregon	RURAL	8.48	0.84	2.42	n/a

Acrolein Study Design

- Experimental Design
  - Variables studied
    1. Canister type and prep (cleaning)
       - Heat vs No-Heat
       - Humidified Air vs Humidified Nitrogen
    2. Lab analysis and calibration gas standards
- Test 1: Blank canisters analysis looking at Acrolein growth
  - Assumption – all SUMMA created equal
- Test 2: PT samples for lab to lab variability


Phase 1 Test 1: Blank Canister Analysis for Acrolein
(corrected values)
1.2
1
0.8
0.6
0.4
0.2
0
ppbv
No Heat
Heat
Day 1
Day 7
Day 14
Day 21
Si/Humid Nitrogen/Heat
SUMMA/Humid Air/No Heat
SUMMA/Humid Nitrogen/Heat
Si/Humid Air/Heat


Phase 2 Test 1: SAT Canisters No Heat vs Heat treated
(corrected values)
1.2
1
0.8
0.6
0.4
0.2
0
ppbv
Day 1
Day 7
Day 14
Day 21
Time
No heat results
(dashed lines)
Same canisters heat cleaned
(solid lines)
Decrease of 20%
Decrease of 120%
Decrease of 220%


Phase 1 Test 2: Acrolein Study PT Samples
(corrected values)
ppbv
1.8
1.6
1.4
1.2
1
0.8
0.6
101%
Bias
High
33%
Day 1
Day 3
Day 7
Day 14
Day 21
Target
SUMMA/Humid Nitrogen/Heat
Fused Si/Humid Air/Heat
Fused Si/Humid Nitrogen/Heat
SUMMA/Humid Air/Heat
SUMMA/Humid Air/No Heat

Labs sent their cal gas in canisters to ORD

		Acrolein Values			Benzene Values		
Lab	**Prep (master cyl conc)**	**Lab**	**ORD**	**% BIAS**	**Lab**	**ORD**	**% BIAS**
Lab 1	Scott (working conc = 2ppbv)	1.87	1.092	-71.25%	4.54	6.607	31.29%
Lab 2	Spectra Gas TO-15 (500ppbv)	0.75	1.225	38.78%	0.89	1.469	39.41%
Lab 3	Spectra Gas TO-15 (1ppmv)	1.03	1.096	6.02%	1.01	1.294	21.95%
Lab 4	Scott (43ppbv)	1.06	0.95	-11.58%	1.06	1.133	6.44%
Lab 4	Spectra Gas TO-15 (100ppbv)	0.9	1.22	26.23%	0.97	1.349	28.09%

Calibrated Flow Controller resulted in better % Bias

Summarize Study results

- Canister prep is a major factor in preventing the growth of Acrolein in canisters.

- Methods procedures need optimize to ensure no growth of Acrolein in canisters.

- Calibration gases play a role in a lab's ability to accurate analyze for Acrolein.

Next Experimental Steps

- Steam Clean canisters per Roy Heaton (RI DOH) procedure.
  - Fill with 1 liter DI H2O, heat to 140°C
  - Remove H2O and clean on cleaning system

- Test H2O extract by Purge & Trap (8260) to see what is being removed.

- Test before and after to quantify effectiveness

What do we do from here?

- Clearly the methodology has issues that affect the ability collect and analyze for Acrolein.

- Lew Weinstock (OAQPS/AAMG) wrote a one pager on recommendations for the data currently in AQS.
  - ➢Create a 2 new bins in AQS called “Unverified Acrolein” and “Verified Acrolein”.
  - ➢ Labs who feel they do Acrolein well, can move data into Verified Acrolein bin.

Our Recommendations for Acrolein by TO-15

- Add heat to canister prep. At least 90°C.

- Test **each** canister for cleanliness **over time** to ensure capability for use for Acrolein.

- Collocate each sampling event.

What about "beyond TO-15" for Acrolein Monitoring?

- Need to develop real time monitoring
- Fit into existing network framework
- Don't require a PhD to operate
- Affordable to populate entire network
- Can we include other carbonyls?

What Steps is EPA doing?

- Working with ORD management
- They have been sending out innovative initiatives for Acrolein research needs
- OAQPS has communicated the method research is needed
- “it’s on the radar screen”, a very high priority on ORD’s project list

Summary

- NATTS see lab to lab variability as seen in PT samples results
- Acrolein study results demonstrated variable results from canisters prep and lab comparisons.
- Canister cleaning should involve testing canisters over time to verify canister is acceptable for sampling Acrolein.

- Discussion and Questions?