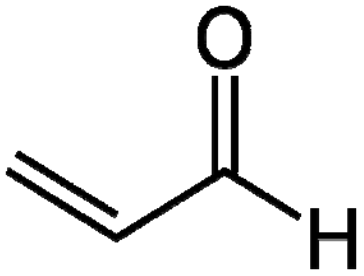
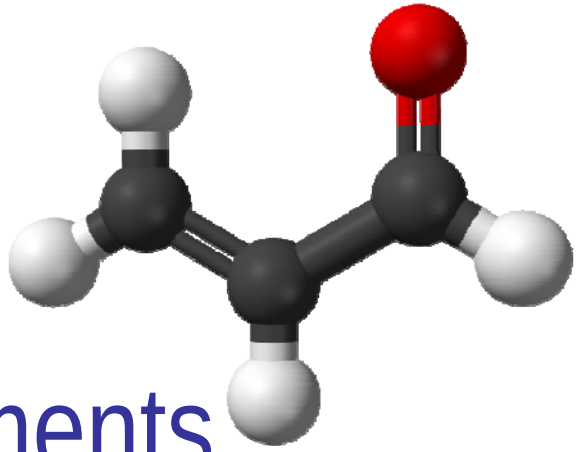




Acrolein Measurements

David Shelow, Joann Rice, Michael Jones, Louise Camalier, USEPA

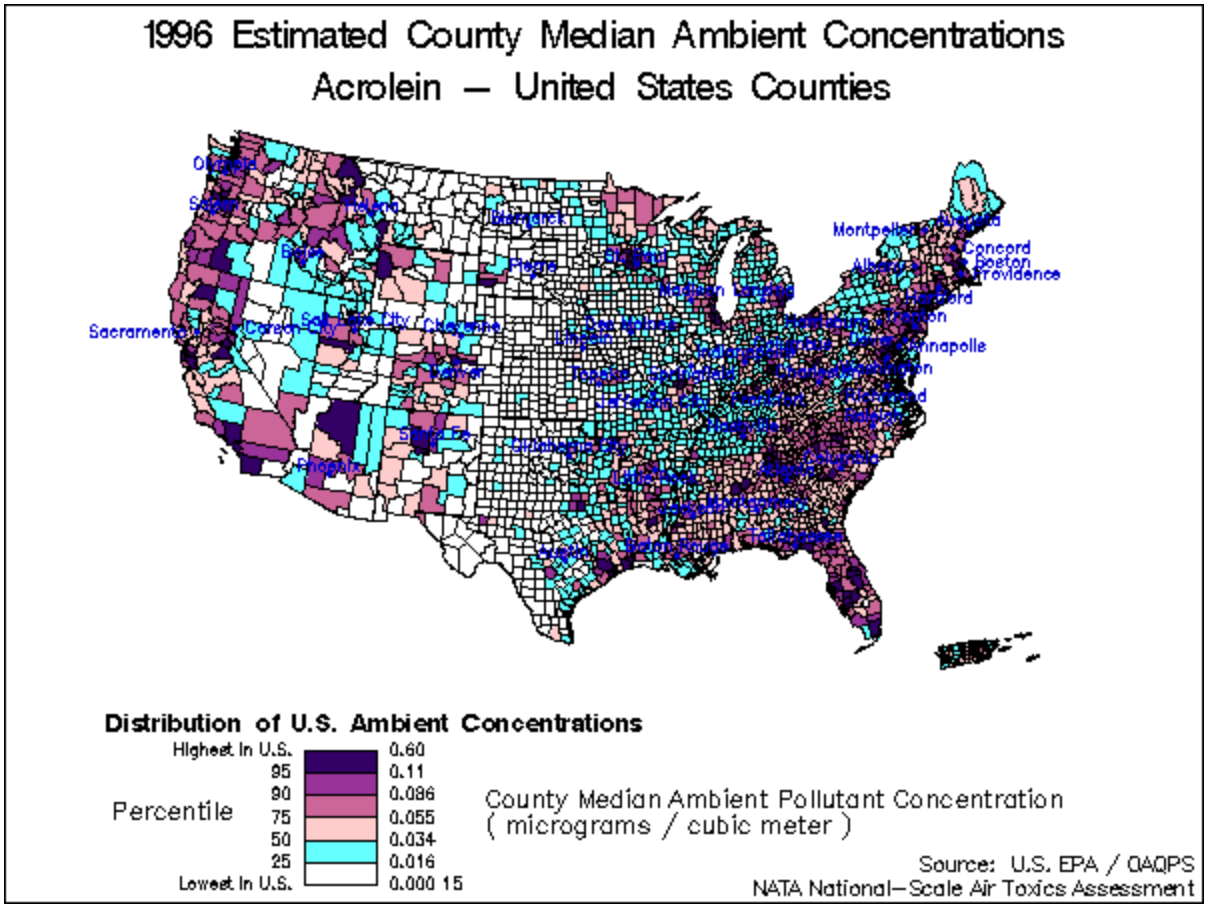
Julie Swift, ERG

Why are we measuring acrolein?

- 2002 National Scale Air Toxics Assessment identified acrolein as a pollutant of concern.
  - Short term screening risk level = 7ug/m3
  - Long term chronic risk level = 0.02ug/m3

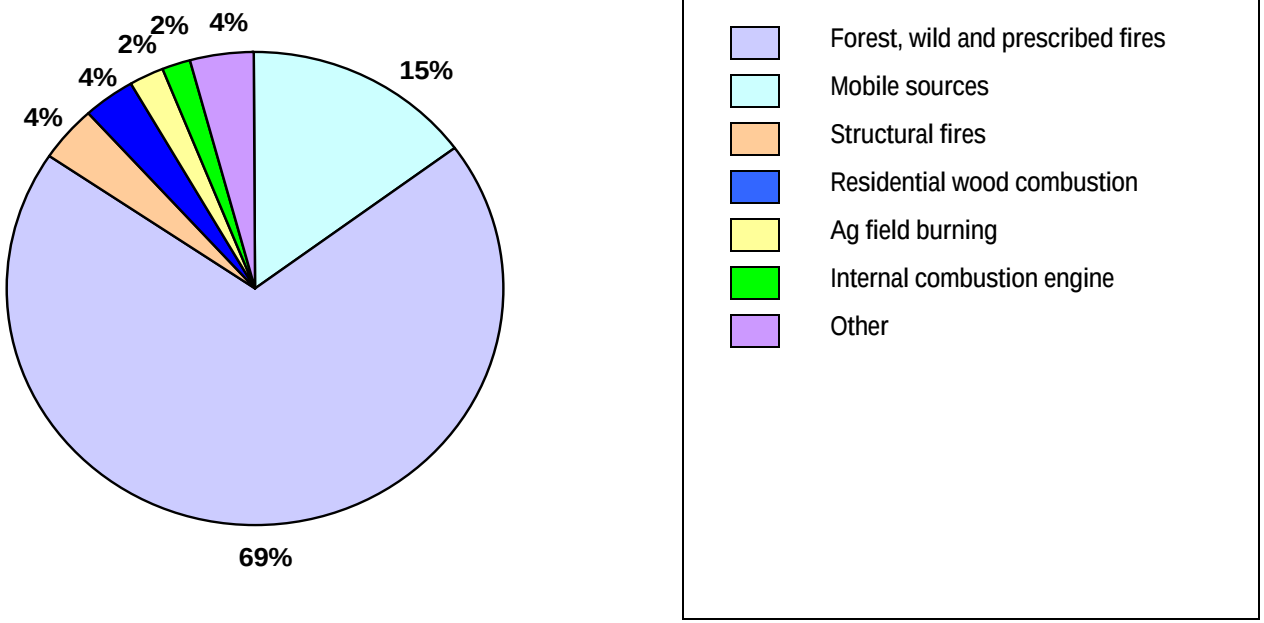
- EPA's Air Toxics monitoring program include measurements of several HAPS (inlcuding acrolein) to provide data for:
  - Future exposure assessment
  - Evaluation of trends
  - Air Quality model evaluations

Ambient Concentrations of Acrolein



Sources of Acrolein

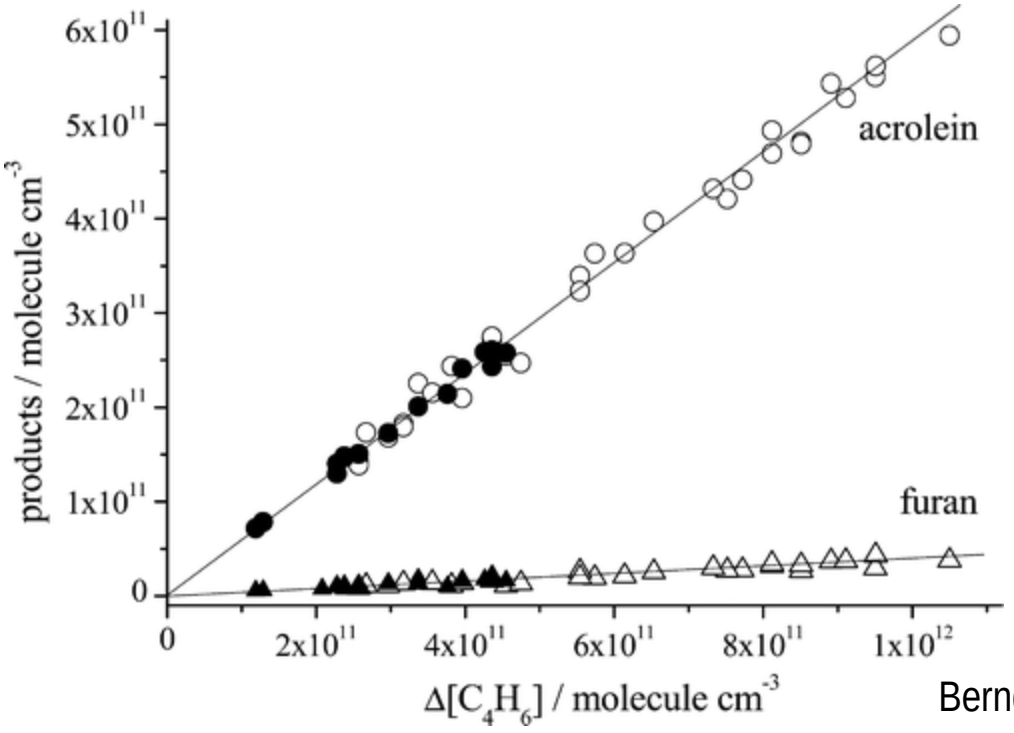
Primary sources



Sources of Acrolein

Secondary sources

- Gas phase reaction of OH radicals with 1,3-butadiene and other aldehydes in presence of NOx.



Berndt et al 2007 J of Phys. Chem

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)

TO-11A DNPH

- EPA Addendum Oct. 4, 2000 Comments from Dr. Robert Lewis TO11A not applicable for acrolein.

- MacGregor et al. documented acrolein-DNPH derivatives unstable

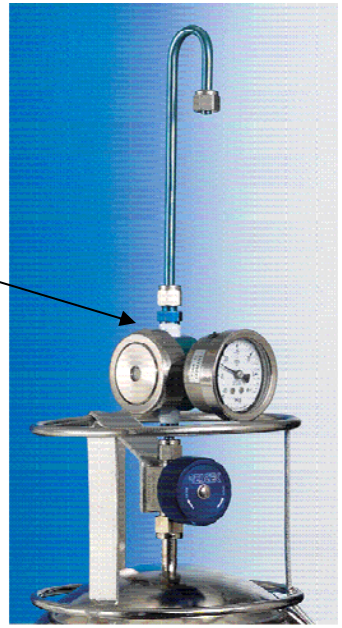
  Decomposition: acrolein-DNPH → unknown

  Reverse reaction: acrolein-DNPH → acrolein + DNPH

TO-15 Sampling

- Subambient (passive) vs Pressurized sampling (non-passive)
- NATTS & UATMP use both
- School Air Toxics (SAT) uses passive (subambient)

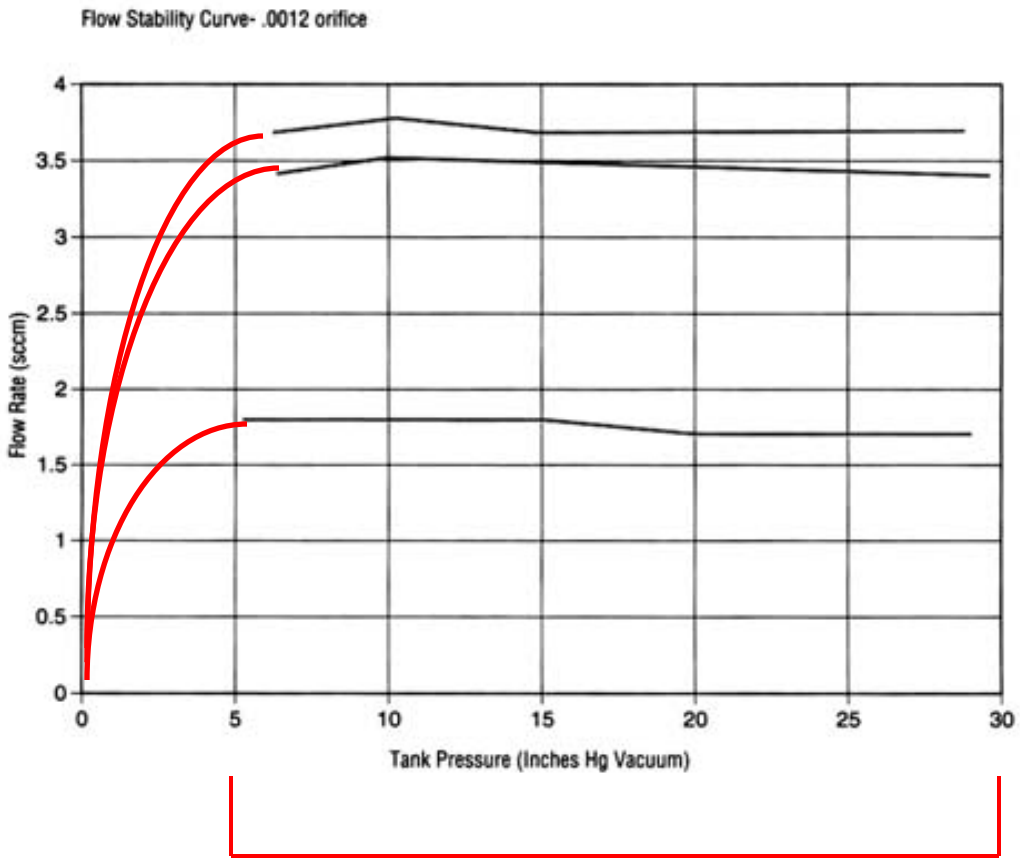
Critical orifice flow controller



Use vacuum of canister to pull sample into canister

Pump and mass flow controller to fill canister, capable of positive pressure

Critical orifice Flow Controller



24 hr sampling period

- Sapphire critical orifice get you in a flow range
- Ability to set flow within the range
- Maintains flows until 5”Hg vacuum
- flexible stainless steel diaphragm for regulating flow.
- Pressure differential

TO-15 Analytical

- Preconcentrator
  - Nafion dryer?
  - Traps
    - Silica Gel
    - Solid Sorbents
    - Good moisture control

- GC/MSD
  - Variety of choices of capillary GC columns
  - Full Scan or Selective Ion Mode
  - Sometimes coupled with other GC detectors

Canister Method Concerns

- "Growth" of aldehydes
  - Short term
  - Long term
- Canister Cleaning procedures
  - Heat vs no heat
- Positive artifact biasing high
  - Interferences and co-elutions
- Analytical methods – Selective Ion Mode (SIM) vs Full Scan mode

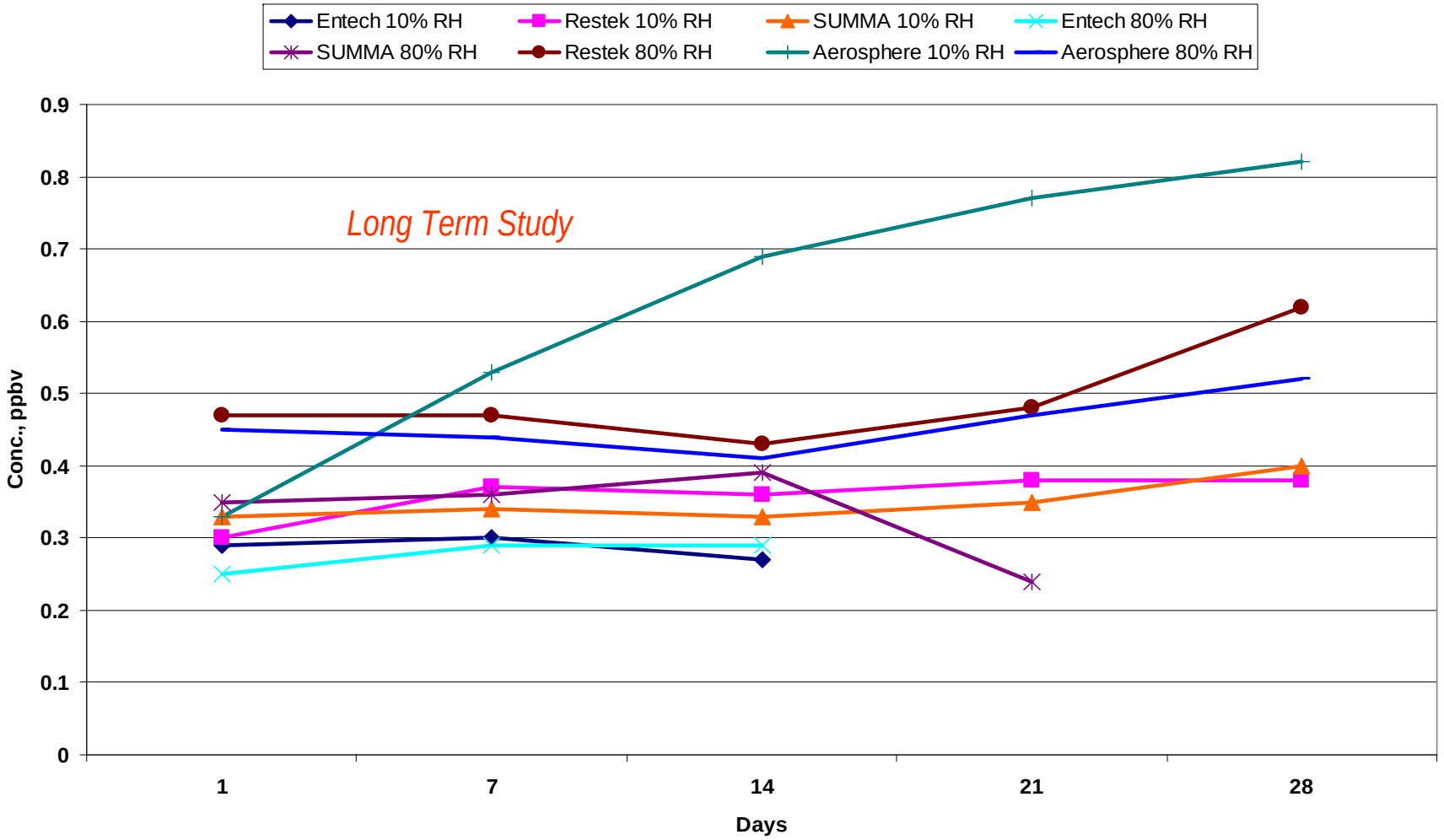
Acrolein stability studies

1. 2005 and 2007 Acrolein data from ERG
   - Long term - 28 day at 10% and 80% RH
   - Standards made in canisters from various manufacturers

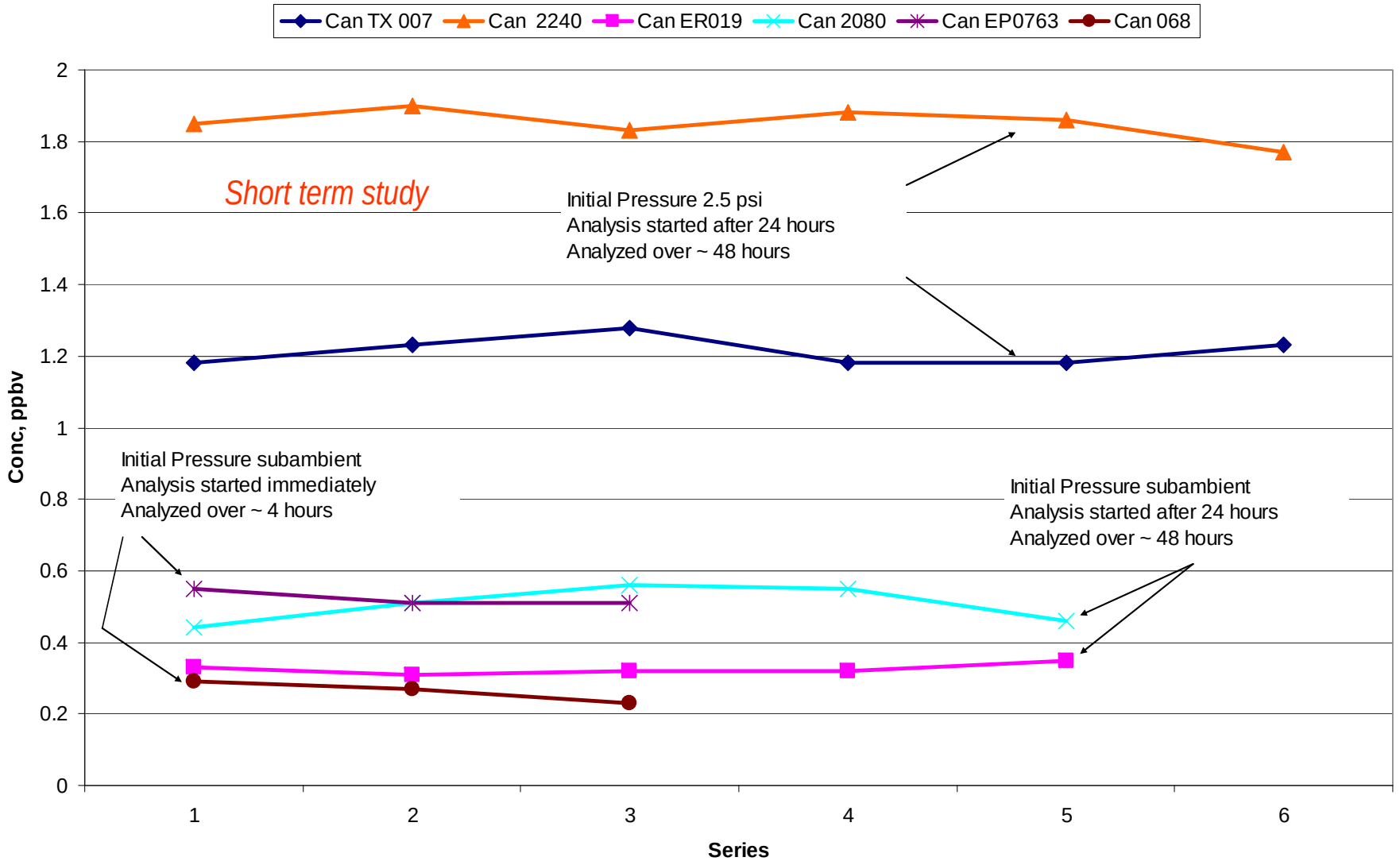
2. Roadway study – Acrolein with 1,3-Butadiene present
   - Ambient air samples RTP, NC
   - Short term – immediately after collecting up to 48 hours

3. School Air Toxics (SAT) canister data
   - Long term

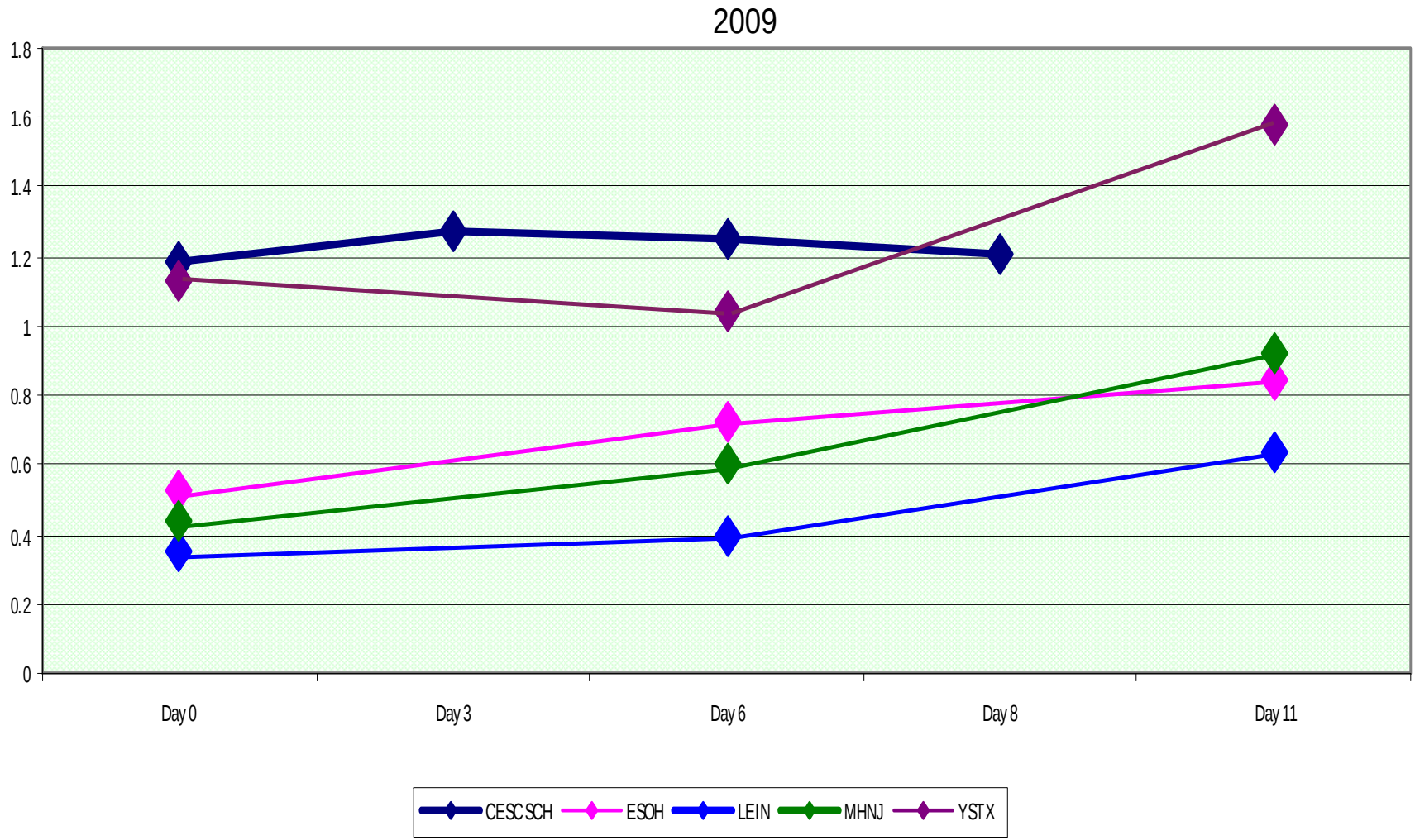
Acrolein in Subambient Canisters with TO-15 Matrix
Prepared at 10% and 80% Humidity



Acrolein Stability of Ambient Air Near Roadway (includes 1,3-Butadiene)



School Air Toxics canisters



Canister cleaning

- Pressure and evacuation - mass dilution
- Humidified air
- Typically 8 hours or more
- Steam Clean - Can add Heat various ways – individually or bulk
- Batch test for blanks – canister that had highest results
  - Blank criteria for cleanliness = 0.20ppbv

Select Ion Mode vs Full Scan mode

Advantages of SIM

Higher sensitivity = Lower detection limit

Reduce interferences with co-elutions

Faster scanning speed

Disadvantages of SIM

No T.I.C

limited # of compounds

Advantages of Full Scan

Complete spectral information for unknowns

T.I.C

Disadvantages of Scan

Lower sensitivity

slower scanning speed

Work ongoing

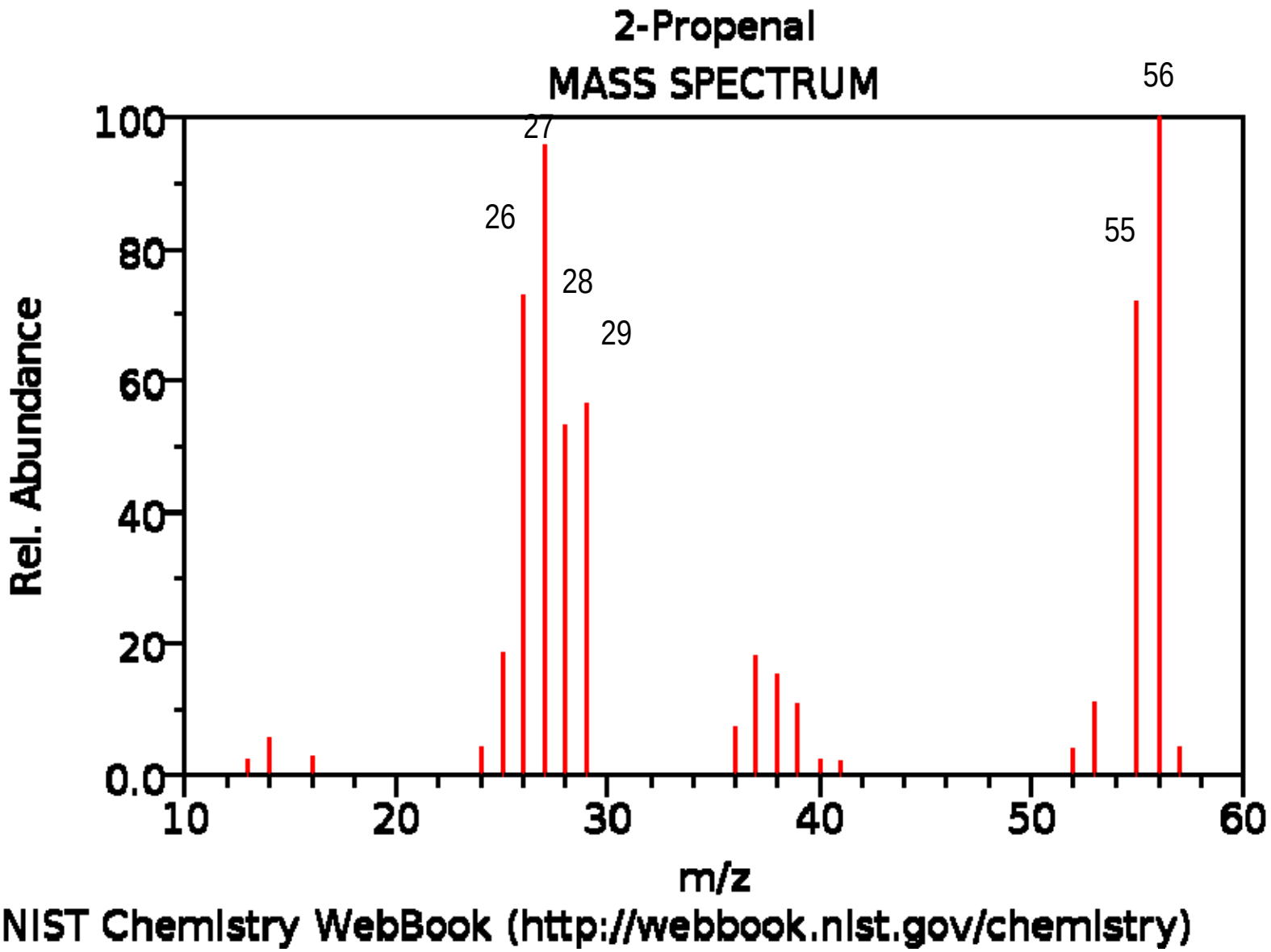
- Short Term
  - OAQPS working with Monitoring agencies to improve canister methods
    - Heat vs no heat during cleaning
    - SIM vs Full Scan analysis
  - EPA Office of Research & Development evaluating DNSH (dansylhydrazine) Cartridges
  - Improved DNPH cartridge coating (Czartech)

- Long Term
  - Cavity ring down spectroscopy
  - MS/MS ion trap
  - Laser induced fluorescence

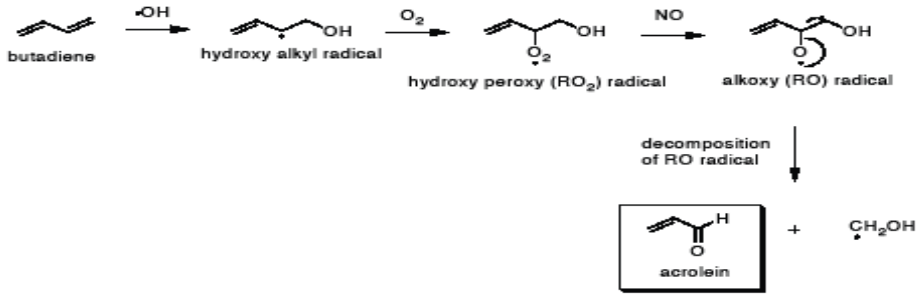
Summary

- TO-15 currently EPA's method of choice for acrolein
  - NATTS, UATMP, SAT
- Concerns with canister based methods can be minimized
  - Canister cleanliness
  - Quick turnaround for analysis
  - Increase sensitivity
- EPA and Monitoring agencies working on TO-15 improvements
- ORD investigating other methodologies

Questions??


2-Propenal
MASS SPECTRUM
Rel. Abundance
m/z
100
80
60
40
20
0.0
10
20
30
40
50
60
26
27
28
29
55
56
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Secondary sources of Acrolein



NOTE: In an urban atmosphere where you have high levels of NOx (i.e., NO), you can generate acrolein easily from butadiene emitted in the atmosphere. Butadiene will react primarily with OH radicals to form an RO radical from the reaction of the intial RO2 radical with anthropogenic NO. The RO radical will will decompose into acrolein and CH2OH radical.

National Air Toxics Summary

- Data in AQS – National database for NATTS and UATMP
- Sort data by method code for VOCs
- Compared canister based vs non-canister based methods
- QA analysis

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	0.08ug/m3

QA data (2006-2009)

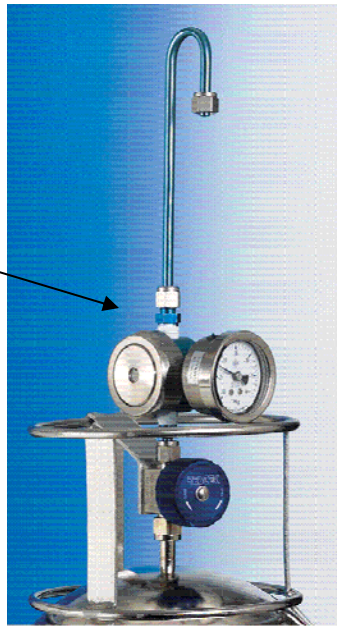
- ERG's NATTS/UATMP Laboratory Precision = 17.58% CV n=695
- ERG's NATTS/UATMP Method Precision = 44.96% CV n=182 pairs
- ERG's Overall Lab Bias = -11.8% PT samples

- SAT Laboratory Precision =
- SAT Method Precision = 44.09% cv n=13

TO-15 Sampling

- Subambient (passive) vs Pressurized sampling (non-passive)

Critical orifice flow controller

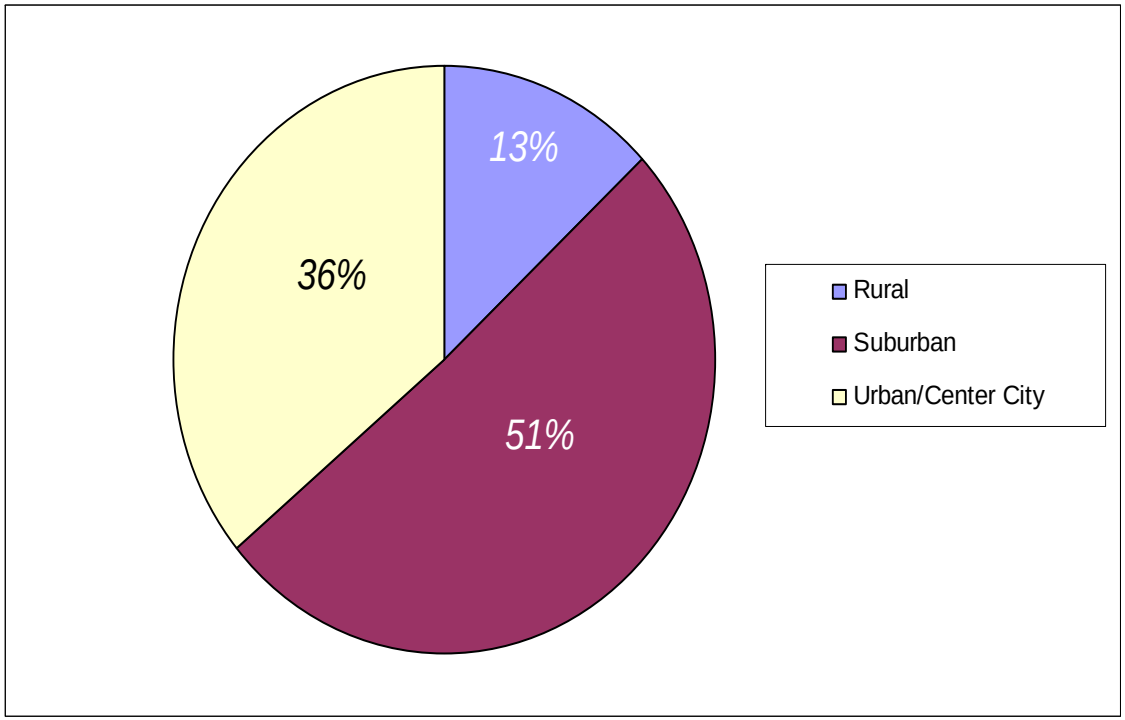


Subambient National Mean = 0.68ug/m3
236 sites

Pressurized National Mean = 0.91ug/m3
287 sites

National Summary breakdown

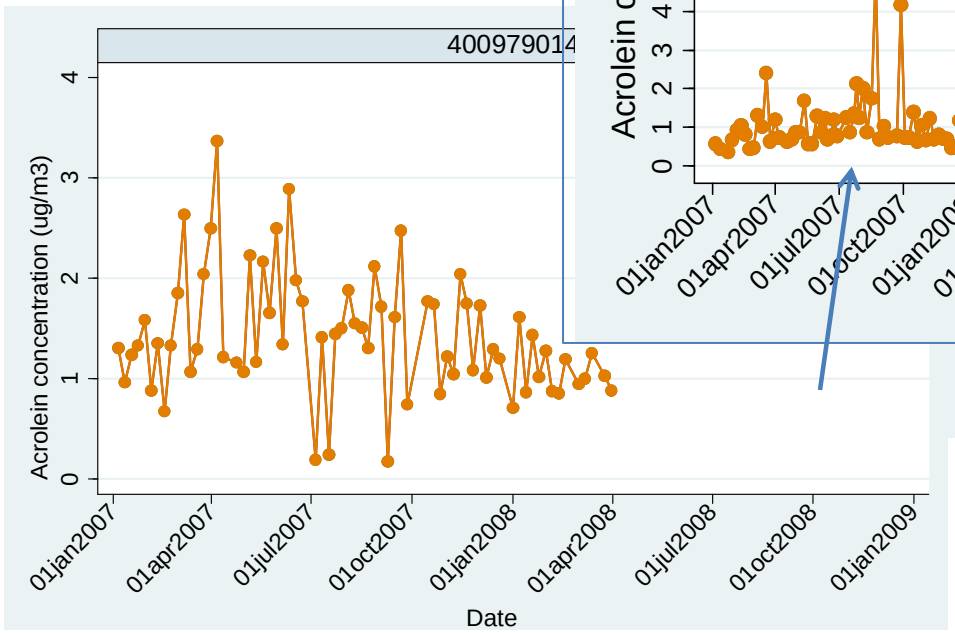
Canister based only

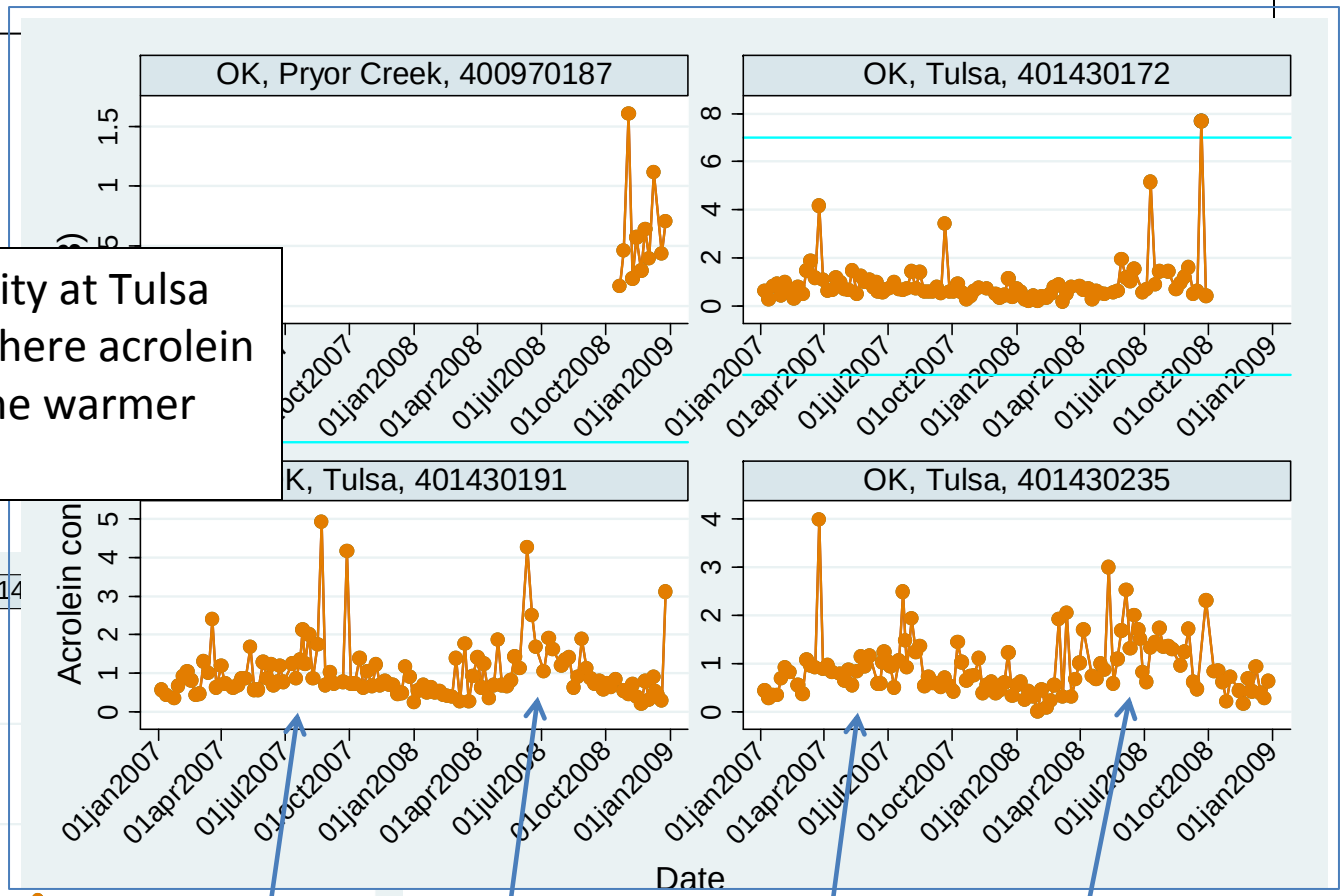


Location	Mean
Rural (74)	*0.50ug/m3*
Suburban (286)	*0.76ug/m3*
Urban (205)	*0.84ug/m3*

Oklahoma

Can see some seasonality at Tulsa sites 0191 and 0235, where acrolein tends to be higher in the warmer months

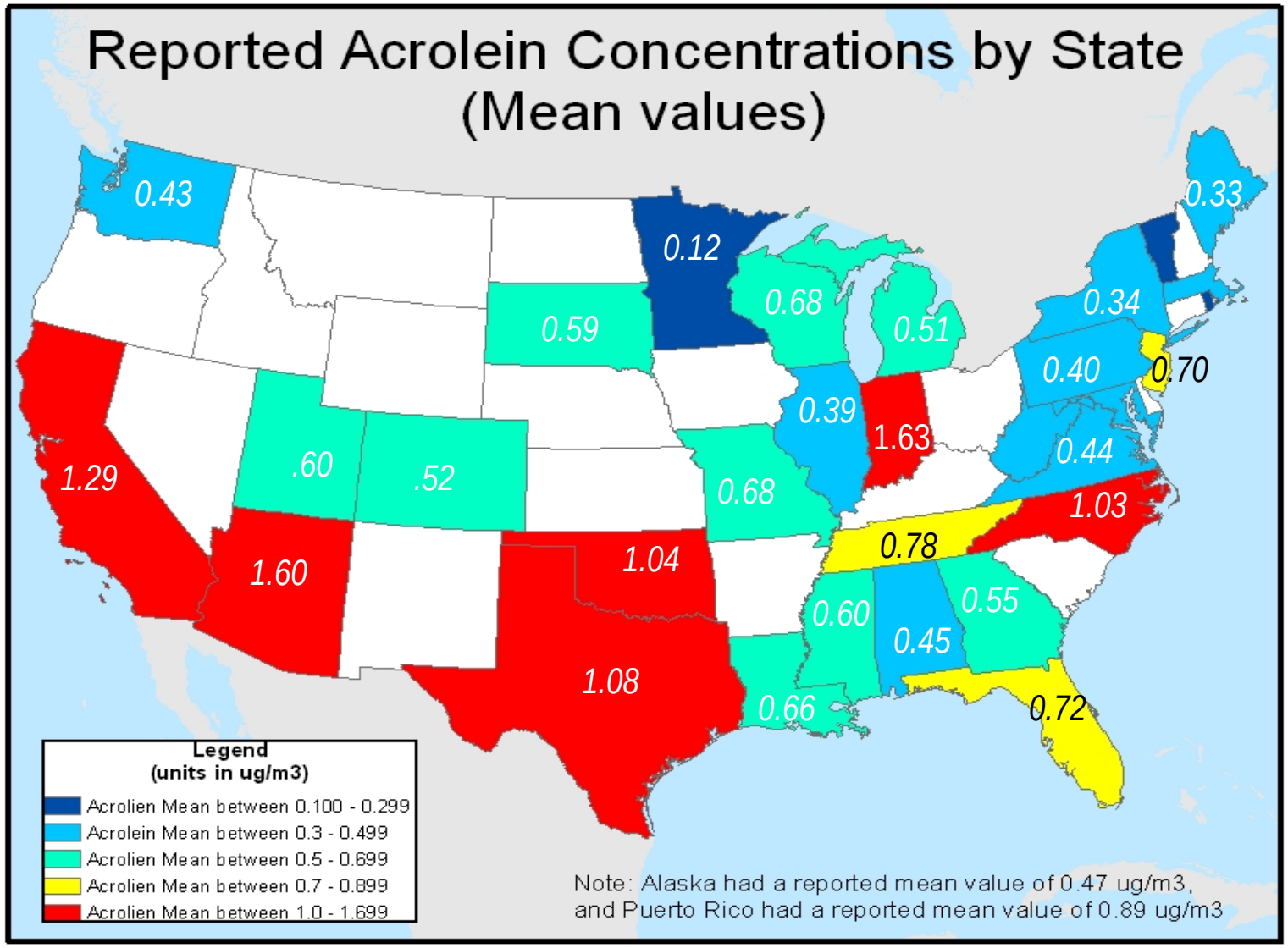




National Air Toxics Summary- Regionally

REGION	method type	Obs	mean	max
01	canister	2746	0.30	4.76
02	canister	1641	0.55	12.32
03	canister	1354	0.44	3.33
04	canister	3732	0.61	20.27
05	canister	2530	1.20	18.24
06	canister	1095	1.04	11.03
07	canister	196	0.68	11.10
08	canister	827	0.57	12.62
09	canister	2417	1.31	23.63
10	canister	269	0.44	3.03
Mexico				
25	canister	52	2.36	12.39

National Air Toxics Summary – By State (year round)



National Air Toxics Summary

- Canister based methods (ug/m3) remove this slide
  - National Mean: 0.77 Max. 23.63 Min.0.00
    - 2006 Obs 3200 Mean: 0.86 Max: 18.24
    - 2007 Obs 5574 Mean: 0.72 Max: 16.43
    - 2008 Obs 6281 Mean: 0.71 Max: 20.27
    - 2009 Obs 1752 Mean 0.80 Max: 23.63
- DNPH Cartridges - Non-Canister based methods (ug/m3)
  - National Mean: 0.08 Max. 12.16 Min. 0.00
    - 2006 Obs 1966 Mean: 0.07 Max: 1.57
    - 2007 Obs 1823 Mean: 0.15 Max: 12.16
    - 2008 Obs 1114 Mean: 0.09 Max: 2.47
    - 2009 Obs 119 Mean 0.03 Max: 0.28