Comparison of Airborne Aldehyde Concentrations Measured by PAKS, TO-15 and DNPH Methods

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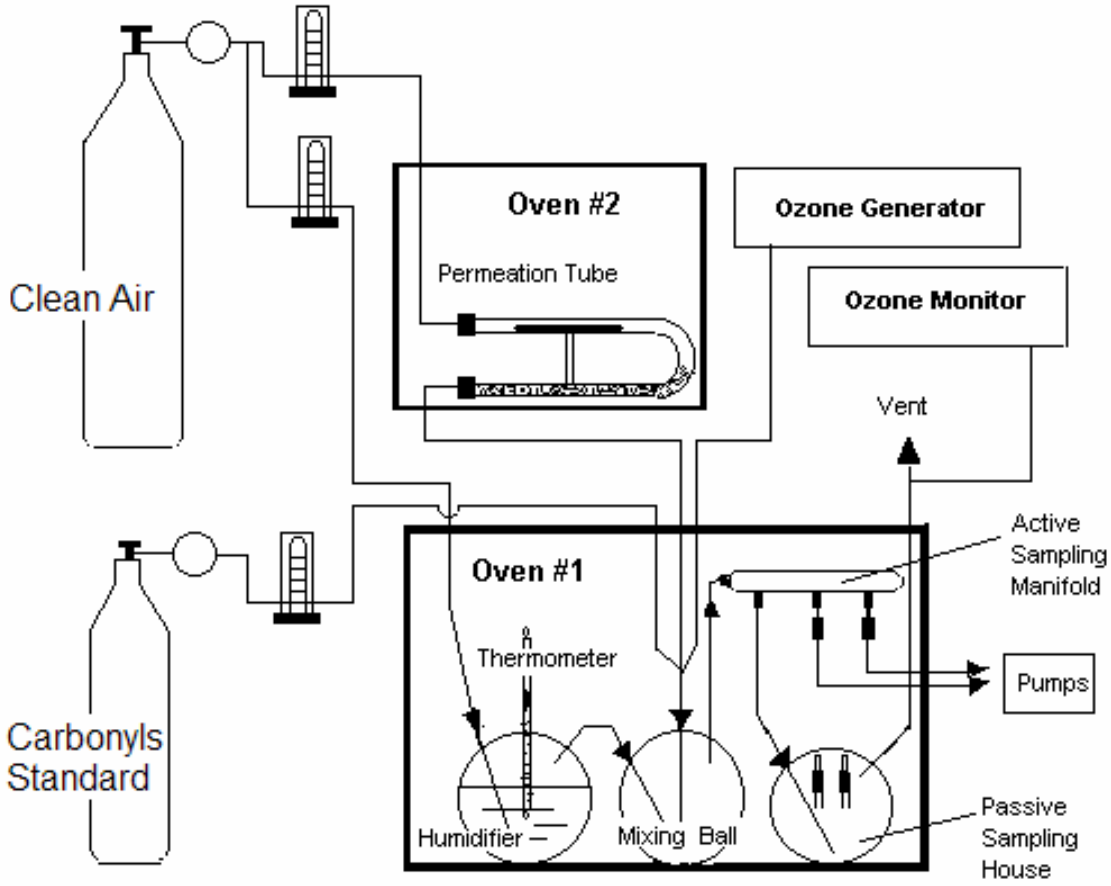
EPA Methods

- **U.S. EPA's Compendium TO-11A**
  - Active sampling with DNPH-coated solid sorbents followed by HPLC-UV measurement technique for carbonyls except acrolein.

- **US EPA TO-15 method for acrolein**
  - **Collection with a canister followed by GC/MS analysis**

Limitations of the TO-11A DNPH Method

- Inadequate collection of unsaturated carbonyls, such as acrolein
- Ozone interferences
- Relative humidity sensitivities
- Inadequate long-term (i.e., ≥ 6 hours) collection of acetaldehyde (Herrington et al., 2007)



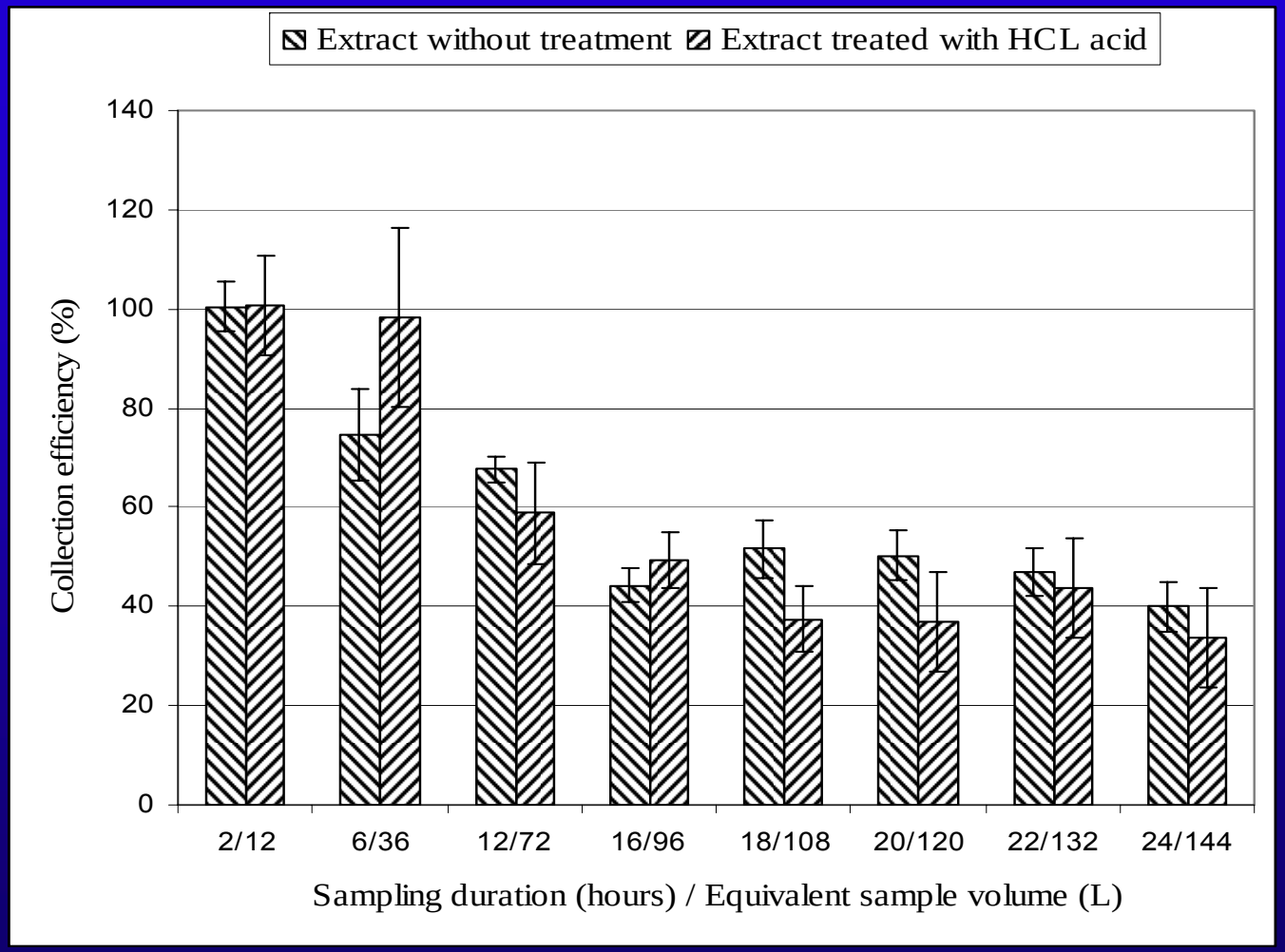
Dynamic atmosphere generation system (Herrington et al. 2007)

Problems w/ DNPH Method- Low Collection Efficiency* for Sampling Time Longer than 6 hours

Experimental condition	Carbonyl	Solid sorbent		
		SUPELCO[a]	WATERS[b]	XPOSURE[c]
3 hours at 30% RH[ef]	Formaldehyde	89 ± 10[g] (3)		
	Acetaldehyde	130 ± 40[g] (3)		
24 hours at 30% RH[ef]	Formaldehyde	85 ± 4 (3)	91 ± 12 (3)	113 ± 4 (3)
	Acetaldehyde	42 ± 7 (3)	48 ± 3 (3)	66 ± 7 (3)
48 hours at 30% RH[ef]	Formaldehyde	91 ± 9 (3)	92 ± 3 (3)	109 ± 20 (3)
	Acetaldehyde	53 ± 23 (3)	43 ± 2 (3)	42 ± 11 (3)
24 hours at 60% RH[eh]	Formaldehyde	100 ± 8 (3)	120 ± 32 (3)	101 ± 13 (3)
	Acetaldehyde	19 ± 3 (3)	21 ± (3)	20 ± (3)

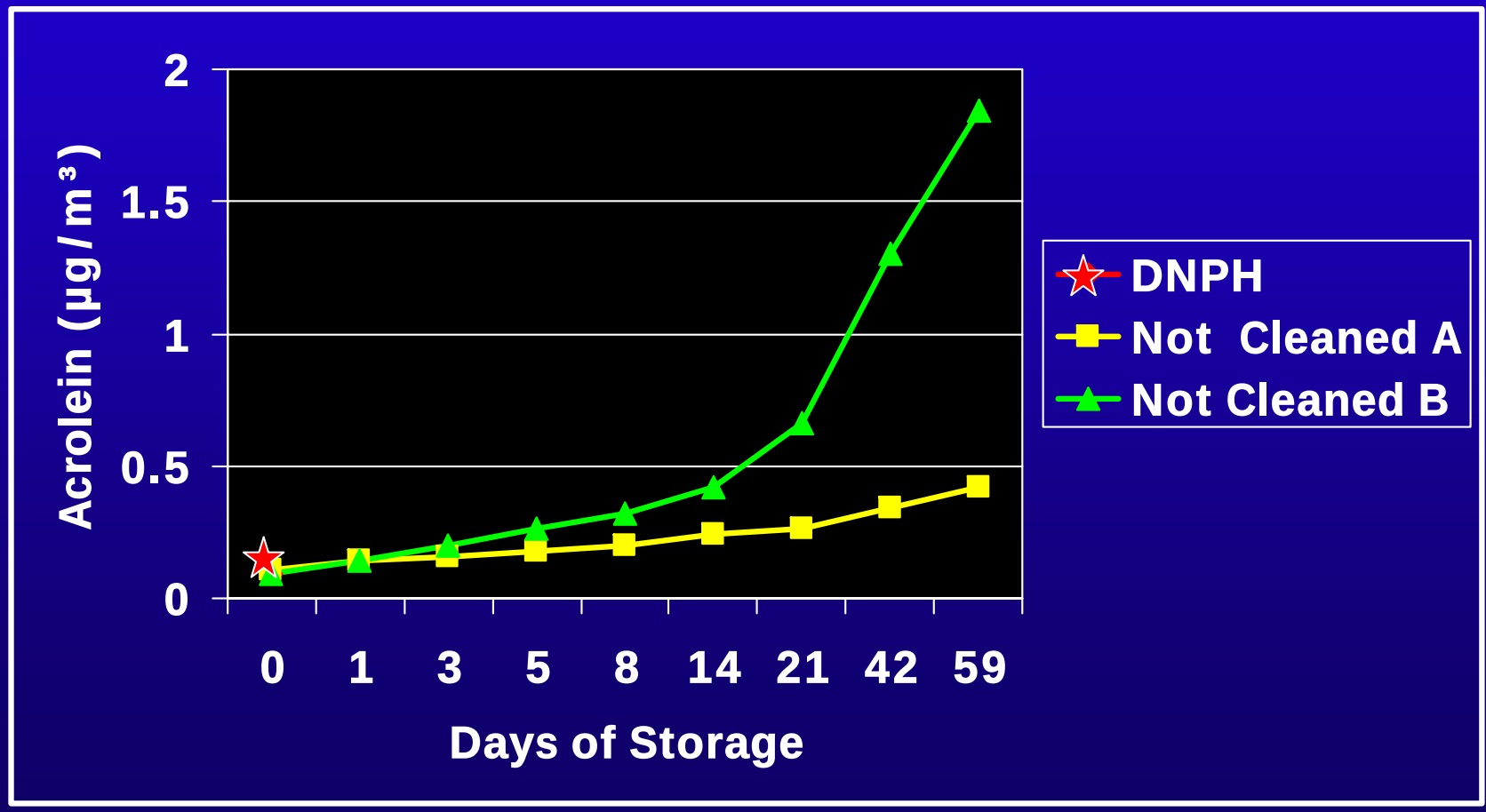
***Ratio of concentration measured to concentration generated in the dynamic dilution system, reported as mean ± sd, parentheses represent sample number (Herrington et al., 2007)**

Collection Efficiency vs. Sampling Duration

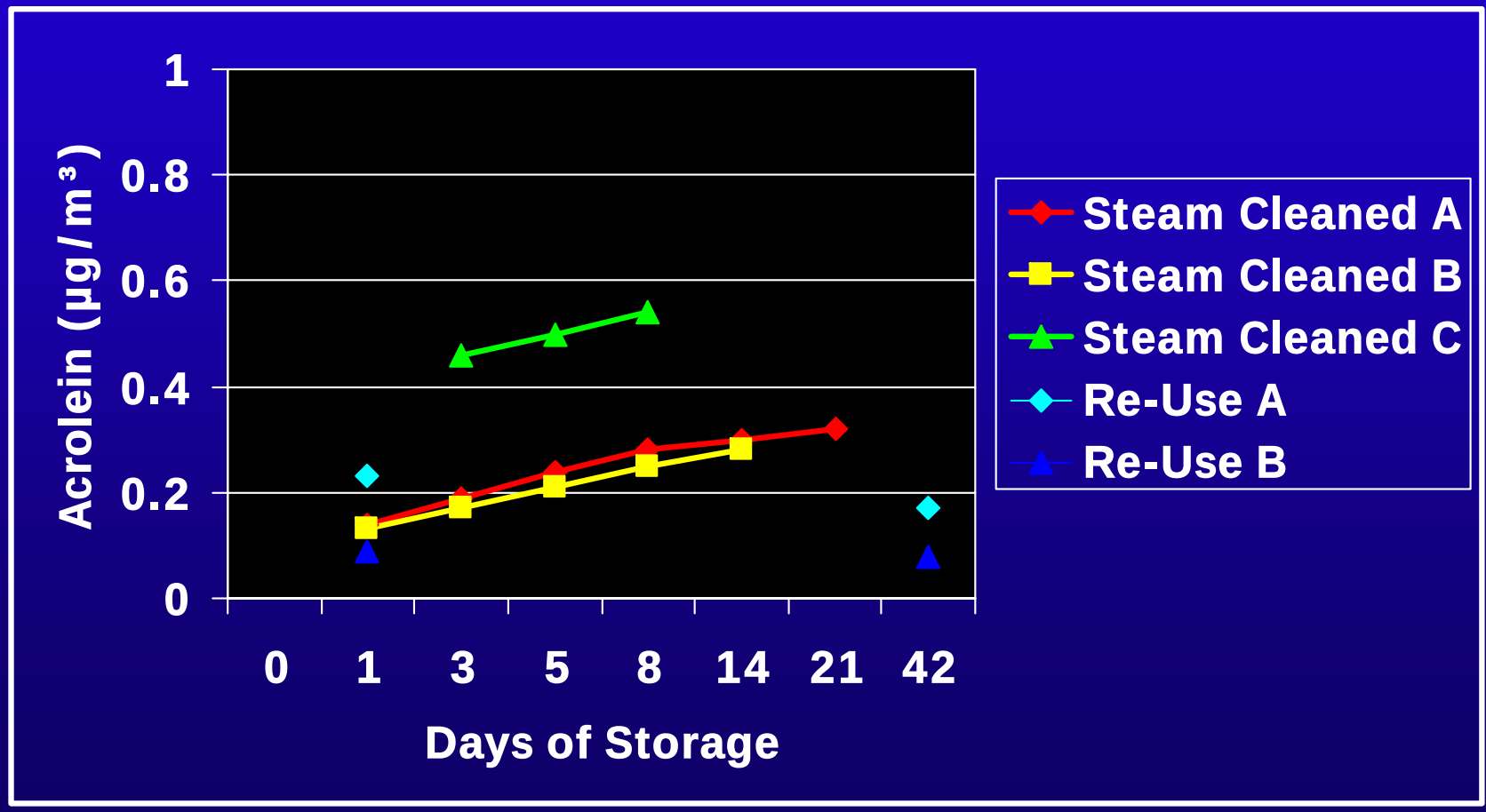


Sampling rate: 100mL/min (Herrington et al., ES&T, 2007)

TO-15 Method for the Measurement of Acrolein Positive Artifact– No Cleaning for the Canister (Dann & Wang, 2007)



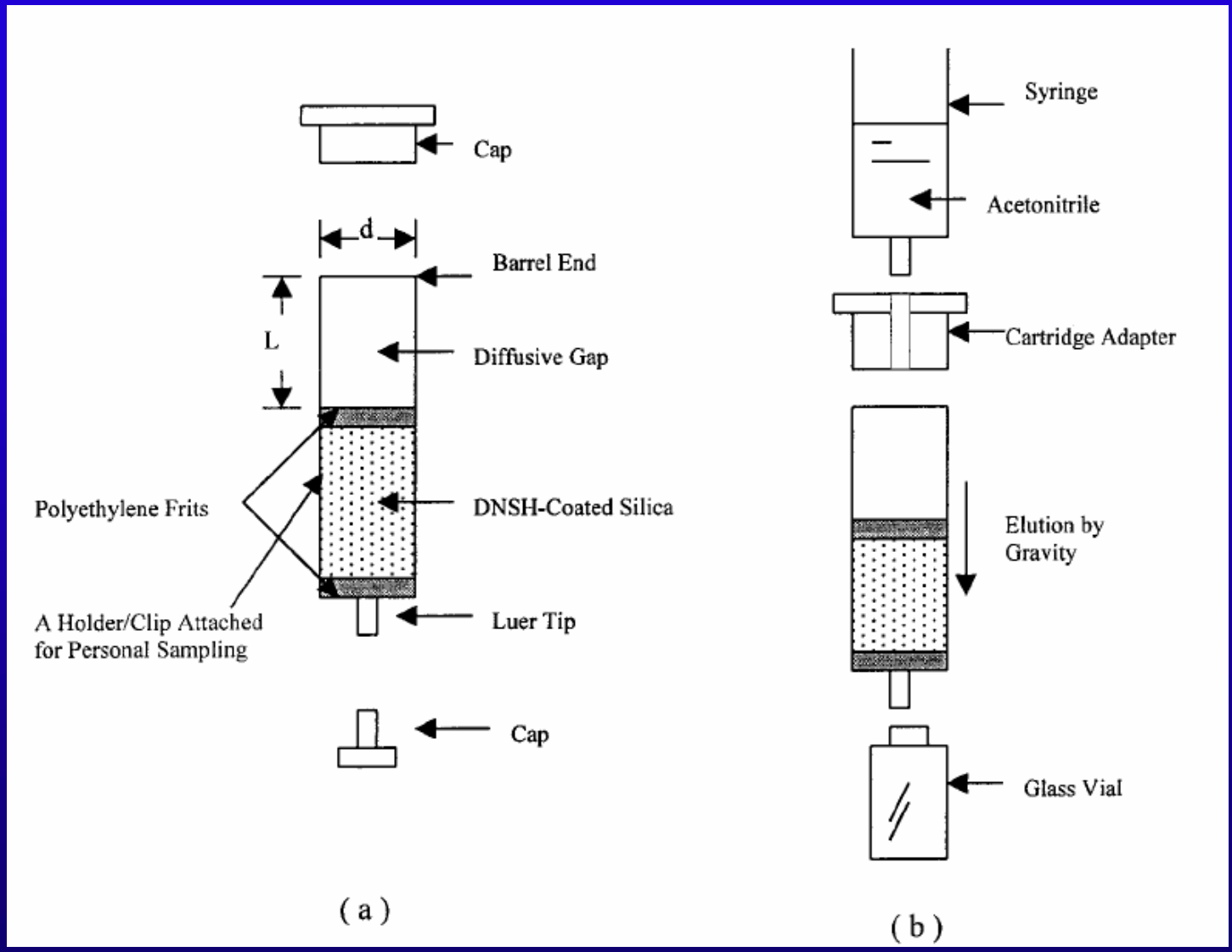
Acrolein Stability in Canisters - with Steam Cleaning (Dann & Wang, 2007)



EOHSI method - Passive Aldehydes and Ketones Sampler (PAKS) Method-Motivation

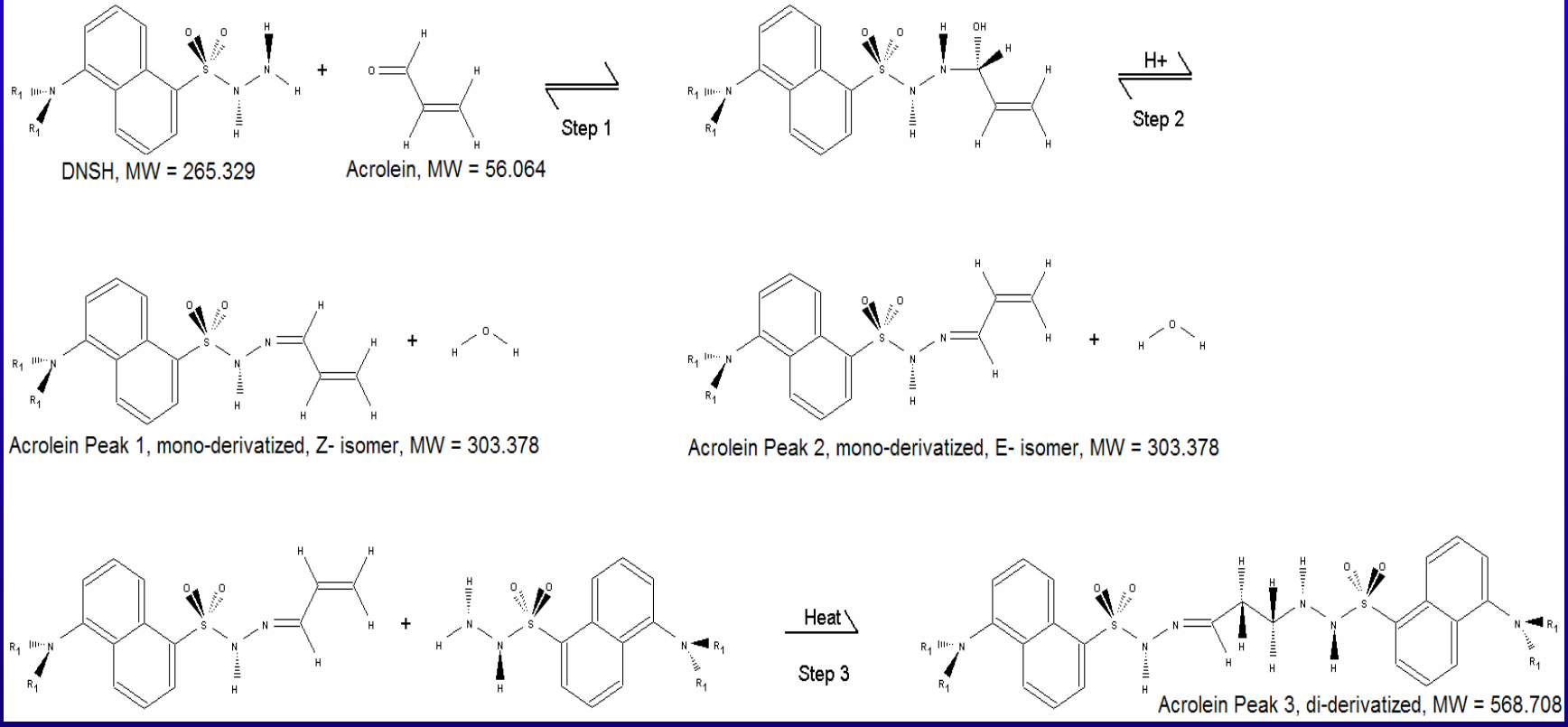
Motivation:

- Develop a passive, sensitive, and accurate method for the measurement of carbonyls in personal air.
- PAKS was developed during the RIOPA(Relationship of Indoor, Outdoor, and Personal Air study).



(a) PAKS configuration and (b) extraction schematic adopted from Zhang et al. 2000.

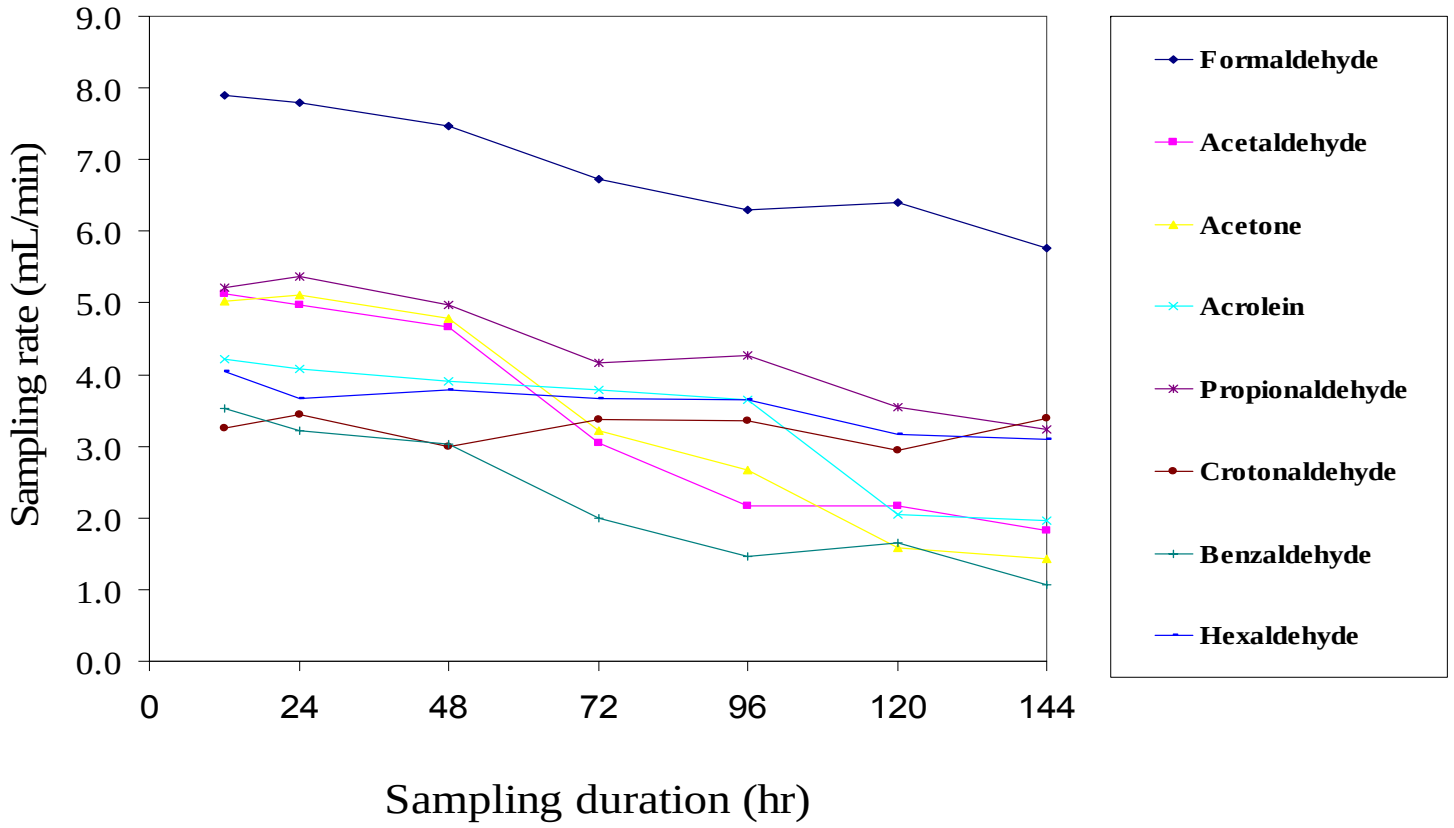
Acrolein-DNSH Derivatization



PAKS Sample Processing

- Baked for 3 hours @ 50°C to promote the carbonyl-DNSH derivatization reactions
- Extracted with 2 mL of ACN
- Analyzed with the HPLC-fluorescence technique

Sampling Rate at Different Sampling Duration



Temperature Effect on Sampling Rate

Carbonyl Compounds	Sampling rate (mL/min)				
	Temperature (°C)			Mean	Maximum difference (%)*
	20	30	40		
Formaldehyde	7.41	7.69	7.74	7.61	4.3
Acetaldehyde	5.15	5.02	5.41	5.19	7.5
Acetone	4.67	4.99	4.97	4.88	6.6
Acrolein	3.87	4.07	4.12	4.02	6.2
Propionaldehyde	4.75	5.23	5.32	5.10	11.2
Crotonaldehyde	3.33	3.54	3.36	3.41	6.2
Benzaldehyde	3.20	3.26	3.41	3.29	6.4
Hexaldehyde	3.68	3.85	4.02	3.85	8.8

•Maximum difference (%) = (Maximum – Minimum) / (Mean) ×100%, based on 9 tests with
•relative humidity = 10%; face velocity = 0.05m/s; and exposure duration = 24hr.

Humidity Effect on Sampling Rate

Carbonyl compounds	Sampling rate (mL/min)				
	Relative humidity (%)			Mean	Maximum difference (%)*
	10	50	90		
Formaldehyde	7.69	7.32	7.23	7.41	6.2
Acetaldehyde	5.02	4.83	4.67	4.84	7.2
Acetone	4.99	5.21	5.12	5.11	4.3
Acrolein	4.07	4.22	4.27	4.19	4.8
Propionaldehyde	5.23	5.44	5.39	5.35	3.9
Crotonaldehyde	3.54	3.68	3.47	3.56	5.9
Benzaldehyde	3.26	3.34	3.16	3.25	5.5
Hexaldehyde	3.85	3.71	3.55	3.70	8.1

*Maximum difference (%) = (Maximum – Minimum) / (Mean) ×100%, based on 9 tests with temperature = 30°C, face velocity = 0.05m/s, and exposure duration = 24hr.

Ozone Effect on Sampling Rate

Conc with Ozone/Conc. without Ozone					
Ozone Conc (ppb)	DNSH	Formaldehyde	Acetaldehyde	Acrolein	Propionaldehyde
50	1.00	0.89	0.94	0.85	0.79
100	0.98	0.94	0.91	0.95	0.86
200	1.00	0.96	1.00	0.88	0.82
300	0.96	0.94	0.81	0.78	0.80
Mean	0.99	0.93	0.92	0.87	0.82
Ozone Conc (ppb)	DNSH	Acetone	Crotonaldehyde	Benzaldehyde	Hexaldehyde
50	1.00	0.82	0.99	1.00	0.80
100	0.98	1.07	0.97	9.60	0.84
200	1.00	1.10	0.93	1.05	0.95
300	0.96	0.95	0.90	0.91	0.91
Mean	0.99	0.99	0.95	0.98	0.88

Field Evaluation and Method Comparison during UCAMPP

- RIOPA, HEI Camden Hot Spot Study, and DEARS
- UCAMPP
  - PAKS vs. DNPH (formaldehyde, acetaldehyde, and propionaldehyde at Chester only)
  - PAK vs. TO-15 (acrolein only)
  - Sampling duration
    - PAKS: 48 hours
    - TO-15 and DNPH: 24 hours

Relative Abs. Percent Difference of Duplicate Samples

(formaldehyde, acetaldehyde, and propionaldehyde)

Compound	Method	N	Mean	STD	Median
Acetaldehyde	DNPH	6	0.13	0.06	0.12
Formaldehyde	DNPH	6	0.17	0.19	0.09
Propionaldehyde	DNPH	6	0.08	0.05	0.08
Acetaldehyde	PAKS	26	0.30	0.26	0.24
Formaldehyde	PAKS	26	0.21	0.15	0.16
Propionaldehyde	PAKS	26	0.52	0.37	0.47

Relative Abs. Percent Difference of Acrolein Duplicate Samples

	N	Mean	STD	Median	%ADL
PAKS	26	33%	33%	29%	100%
TO-15	23	22%	21%	18%	70%

TO-15 Duplicate Date

C1(ug/m^3)	C2 (ug/m^3)	Diff %
0.07	**0.07**	**0.0**
0.25	**0.25**	**0.0**
0.25	**0.25**	**0.0**
0.25	**0.25**	**0.0**
0.25	**0.25**	**0.0**
0.25	**0.25**	**0.0**
0.25	**0.25**	**0.0**
1.06	1.31	11
0.30	0.23	13
0.44	0.32	15
0.53	0.53	0.0

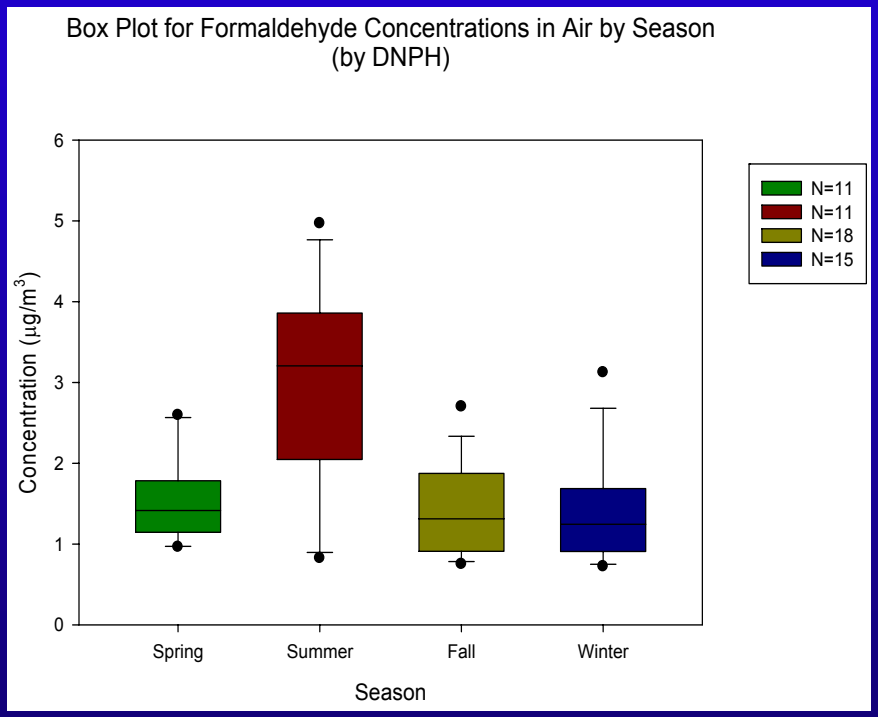
C1(ug/m^3)	C2 (ug/m^3)	Diff %
1.15	0.80	18
0.71	1.03	18
1.36	0.67	34
0.51	0.25	35
0.67	1.38	35
0.21	0.44	36
0.44	0.96	38
0.55	0.25	38
0.41	0.96	40
0.57	1.45	43
2.00	0.69	49
1.61	0.25	73

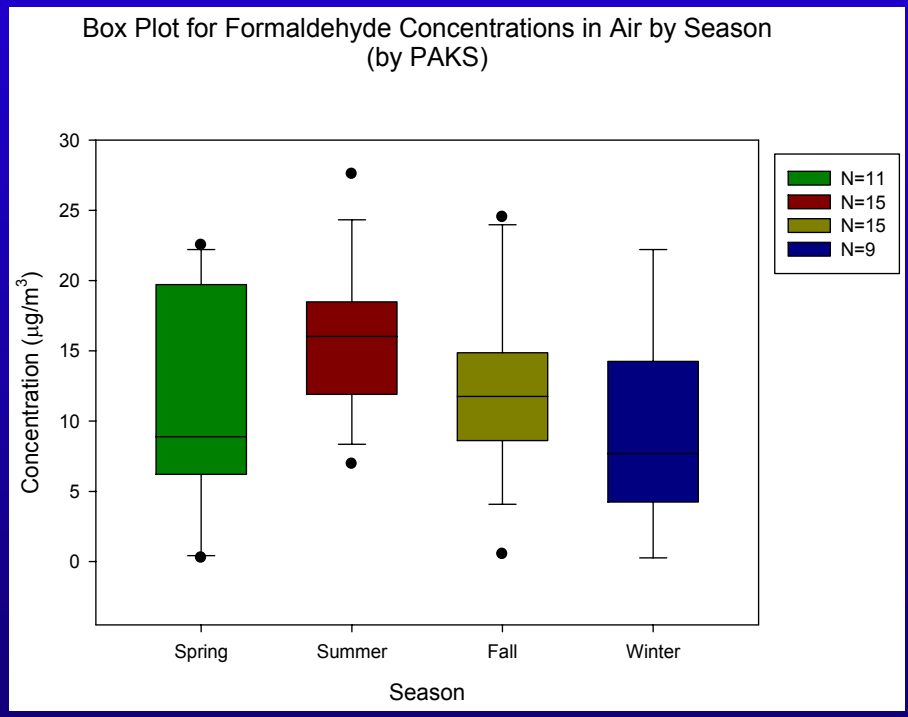
PAKS Duplicate Data

C1 (ug/m^3)	C2 (ug/m^3)	%diff
0.466	0.467	0.002
1.16	1.19	0.02
0.23	0.24	0.04
1.16	1.11	0.04
2.38	2.29	0.04
0.72	0.75	0.05
1.81	1.68	0.07
0.52	0.47	0.11
1.35	1.21	0.11
0.44	0.50	0.12
1.57	1.90	0.19
1.20	1.47	0.20
0.64	0.81	0.24

C1 (ug/m^3)	C2 (ug/m^3)	%diff
0.14	**0.20**	**0.35**
0.77	1.14	0.38
0.88	1.31	0.39
0.48	0.32	0.40
1.13	0.75	0.40
0.17	**0.28**	**0.47**
0.79	1.53	0.64
0.86	0.43	0.67
0.29	0.64	0.76
0.16	**0.44**	**0.96**
0.19	**0.04**	**1.33**

PAKS vs. DNPH (Formaldehyde at Chester Site) - by Season

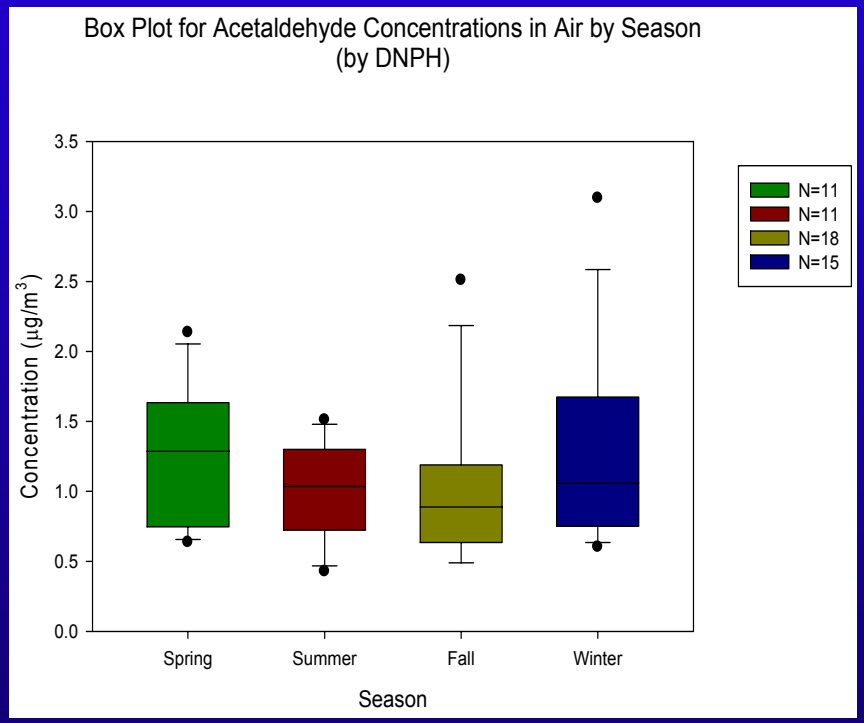


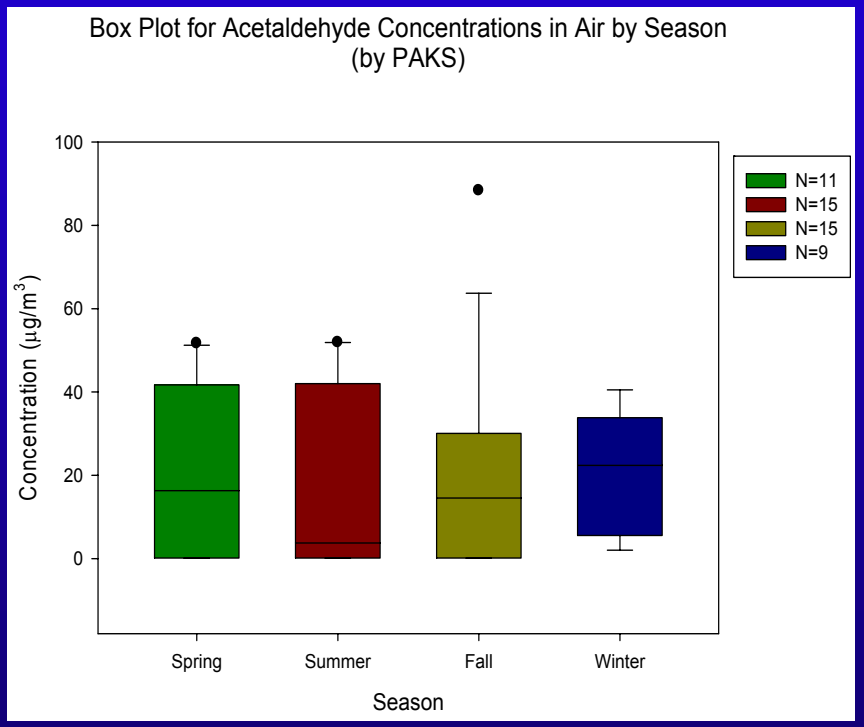


DNPH: P=0.0065

PAKS: P=0.06

PAKS vs. DNPH (Acetaldehyde at Chester Site, NJ) - by Season

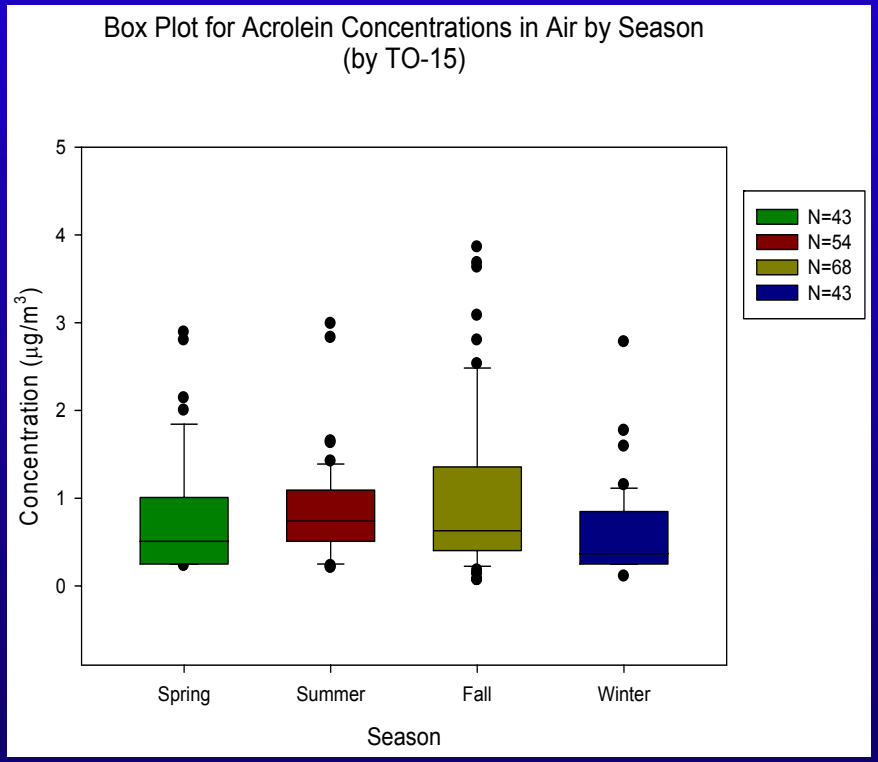


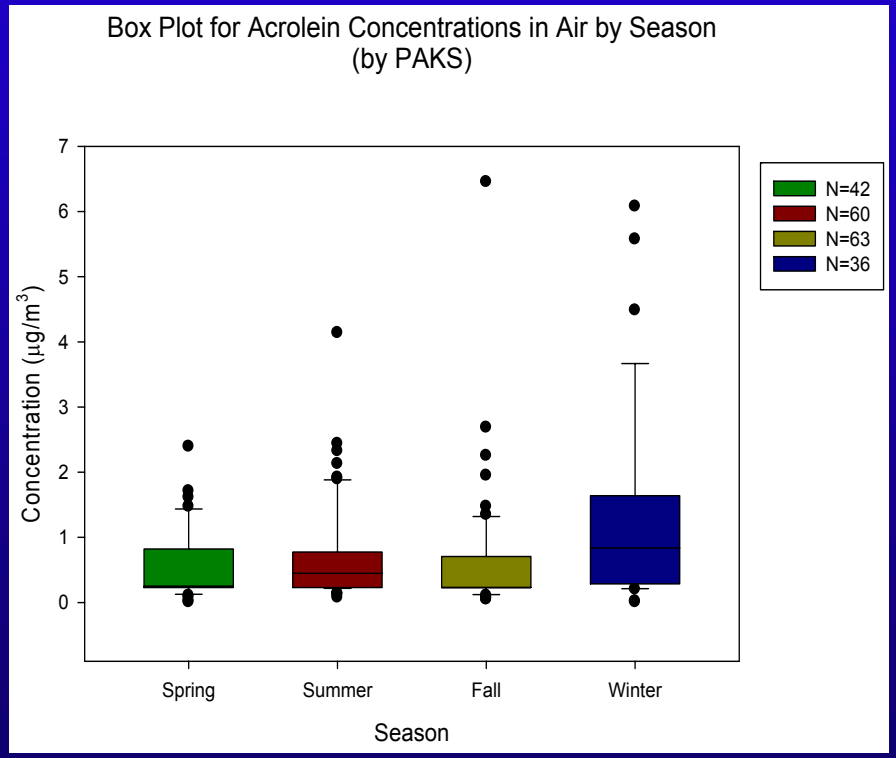


DNPH: P=0.46

PAKS: P=0.90

PAKS vs. To-15 (Acrolein) -by Season

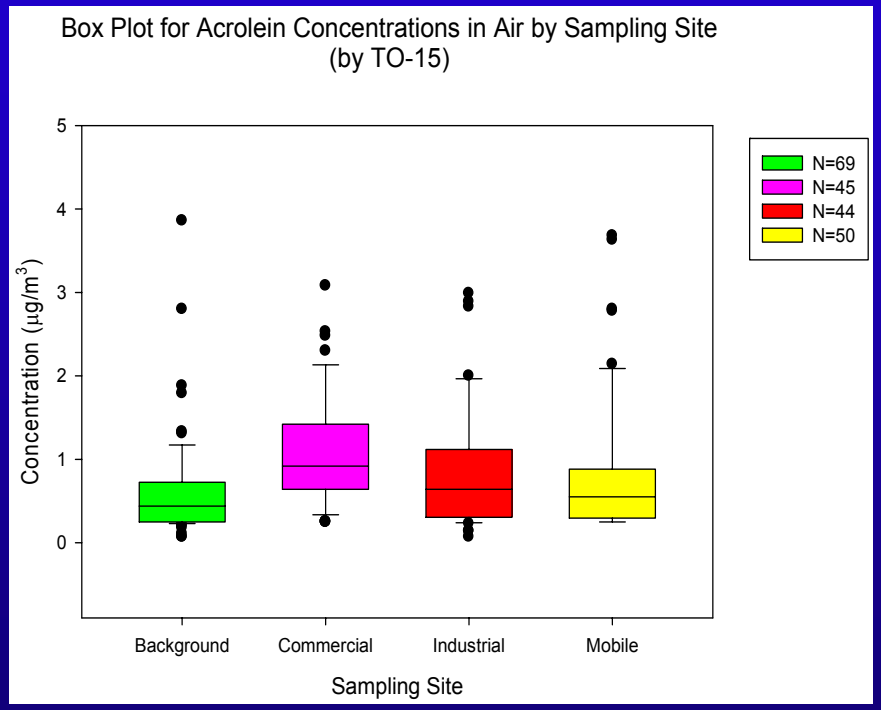


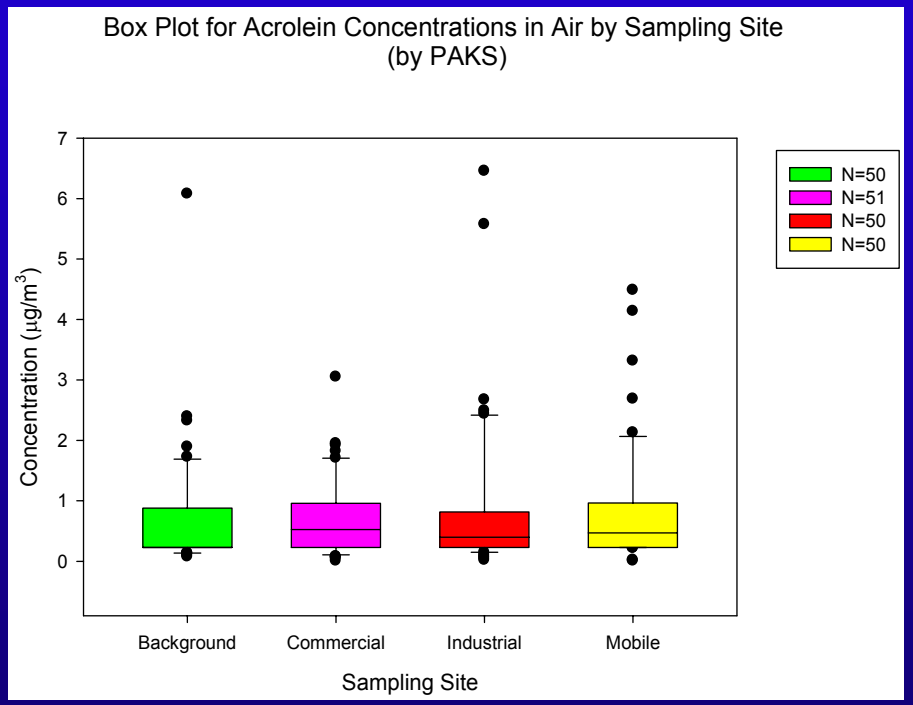


TO15: P=0.0194

PAKS: P=0.003

PAKS vs. To-15 (Acrolein) - by Site





TO-15: P<0.0001

PAKS: P=0.317

Conclusions and Recommendation

PAKS (DNSH-HPLC/fluorescence)

- Passive, sensitive, no ozone interferences, adequate collection of unsaturated carbonyls, and adequate long-term collection of carbonyls.
- High background and large variability but can be reduced by collecting one field blank during each sampling day.

TO-15 Canister-GC/MS method

Good precision but stability and sensitivity need to be evaluated and improved (e.g. spiking samples with synthetic air mixture)

TO-11A (DNPH-HPLC/UV)

Good precision but collection efficiency for sampling time >6 hours needs to be evaluated for carbonyls.

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