California Environmental Protection Agency

Air Resources Board

INTERLABORATORY COMPARISON OF AMBIENT AIR SAMPLES

Presented by
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Interlaboratory Comparison of Ambient Air Samples

- Supports both the PAMS hydrocarbon and Toxics programs.
- One of many Quality Assurance tools used to assess data quality and evaluate laboratory practices.

Three Quality Assurance Tools

- Laboratory audits
  - Round robin comparison
  - Using NIST-traceable cylinder
- Through-The-Probe (TTP) audits
  - Using NIST-traceable cylinder introduced into air monitoring station via TTP
  - Cylinder diluted to various concentrations
- Interlaboratory comparison
  - Using real-world samples
  - Ambient level concentrations

Interlaboratory Comparison Check Progression

- Year 1997 (*First Year Conducted*)
  - Focused on Hydrocarbon (NMHC) species
  - 5 laboratories participated
  - ARB, Districts, Research
- Year 2000
  - Expanded to include Toxics species
  - 3 laboratories participated
  - ARB, Districts, Research
- Year 2004 Comparison
  - Improved equipment capabilities
  - 14 laboratories participated
  - Nationwide laboratory participation

Interlaboratory Comparison of Ambient Air Samples

- Assess the variability of the measurement process :
  - Using real-world samples
  - Ambient level concentrations
  - Similar to round robin comparisons
  - Not indication of accuracy

Cost Effective Procedure

- Cost effective Quality Assurance procedure
  - Each lab will produce one clean canister and perform analysis once can is filled.
- Compared to cylinder round robin
  - NIST-certified cylinders are quite costly.
  - Shipping of compressed gas cylinders can be expensive and timely.

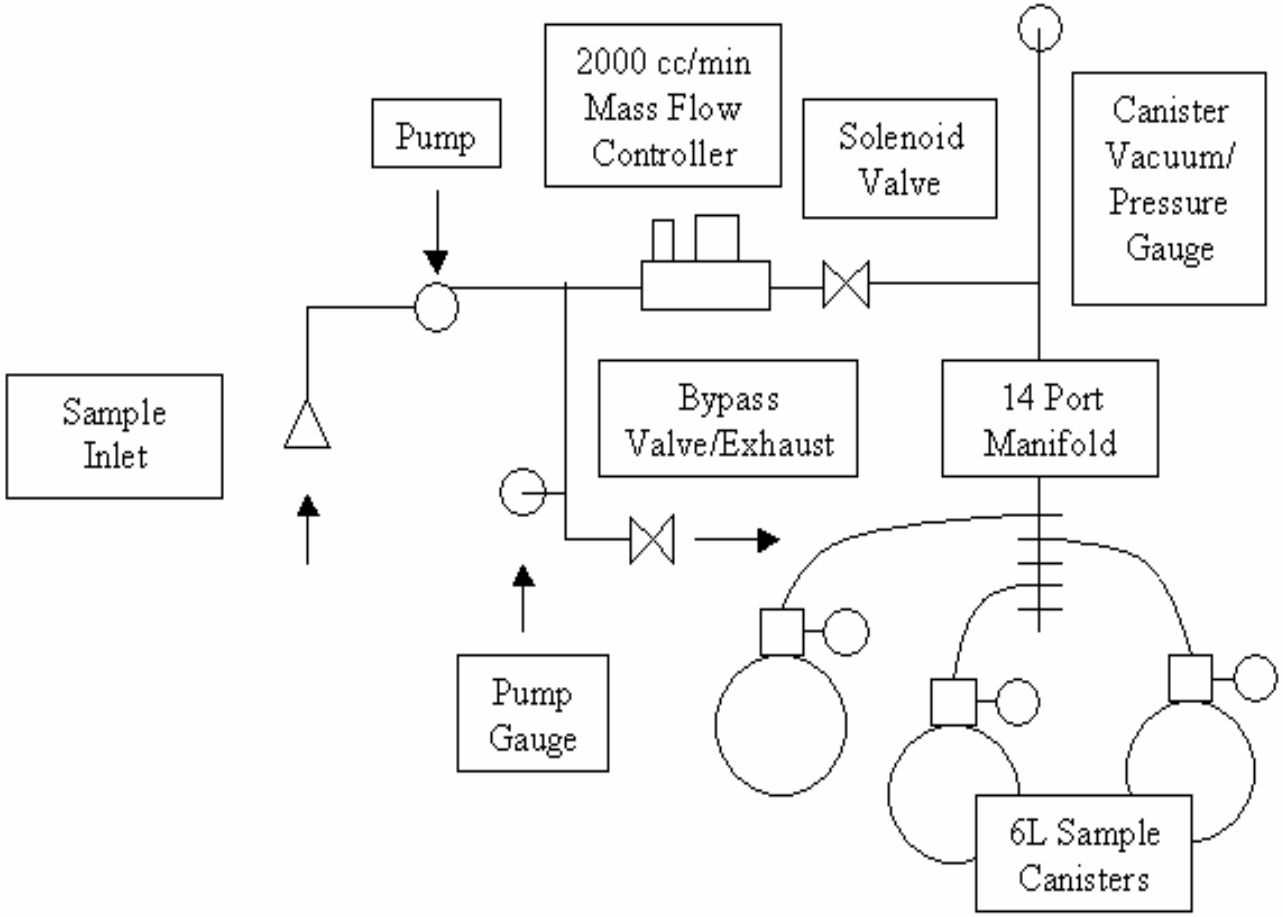
Sampling Methodology

- Modified round-robin
- Canister sampler
  - Simultaneous collection
  - Custom-built manifold
  - Ports for 14 canisters
- Sampling location
  - PAMS site/Toxics site
  - Historically high NMHC/Toxic concentrations
- Sampling time
  - For PAMS, sample during season
  - Collect samples during peak hours to capture highest concentrations

Ambient Air Collection Equipment

- Canister sampler (RMESI 910A) modified to fill up to 14 canisters simultaneously
- Stainless steel probe
- Stainless steel tubing and fittings
- One 6L sample canister sent from each participating laboratory
- Canister rack capable of holding 14 cans
- Barometer, Temperature and RH sensors

Modified Canister Sampler



Pre-Sampling Coordination

- Pre-Sampling Tasks (4 weeks before sampling date)
  - Sampling location and participants are determined
  - Sampling system cleaned and verified
- Set-Up (1 day before sampling date)
  - Probe set-up and position
  - Leak check
  - Internal air purge
- Operation
  - Flow rate varies
  - Final pressure consideration

Pre-Sampling Leak Check

- Sampling system held under vacuum to insure leak-free sampling system :
  - Record each canisters vacuum
  - If vacuum is maintained for 15 minutes, system is verified leak-free
  - If vacuum cannot be maintained by sampling system, troubleshooting is required

Establish Sampler Flow Rate

- The sampler flow rate is derived using the following equation:

$$F=N[(P)(V)]/(T)(60)$$

Where:

F = flow rate (cc/min)
N = number of canisters
P = final canister pressure (atm)
V = total volume of all sample canisters (cc)
T = desired sampling time (hrs)
60 = conversion factor (min/hr)

System Operation

- Once system is verified leak-free, sampler is turned on and allowed to perform it's mandatory internal air purge
- Adjust sampler flow controller to desired flow rate
- Open all canister valves and begin drawing ambient air into the sample canisters

Post-Sampling

- After desired sampling period has elapsed, close all canister valves, record each canister's pressure and turn the sampler off.
- Remove each canister from the supply lines, cap sampler ports and presentation lines to prevent contamination.
- The filled canisters are returned to their respective laboratories for analysis and each laboratory is requested to submit their analysis results to the QAS within 10 working days.

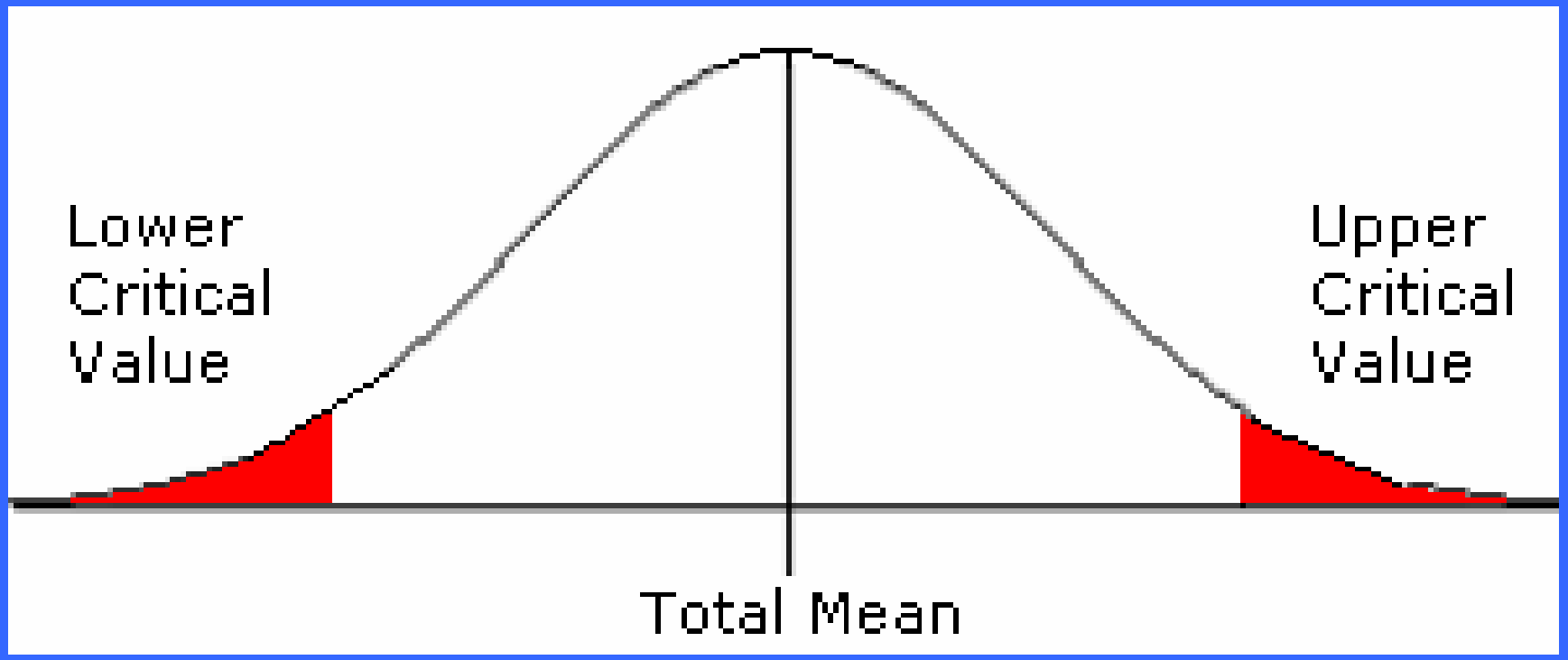
Data Analysis

- All compounds are included in comparison if detected by more than two laboratories.
- Tabulate all responses above the labs LOD.
- Calculate total average and standard deviation for each compound
- Establish critical values

Establishing Critical Values

Lower Critical Value = St Dev x 1.28 - mean

Upper Critical Value = St Dev x 1.28 + mean



Calculating an Adjusted Mean

- All values that fall within the critical value limits will be included in the adjusted mean and standard deviation calculations.

- An adjusted mean and standard deviation are calculated for each compound.

Comparison Data Table

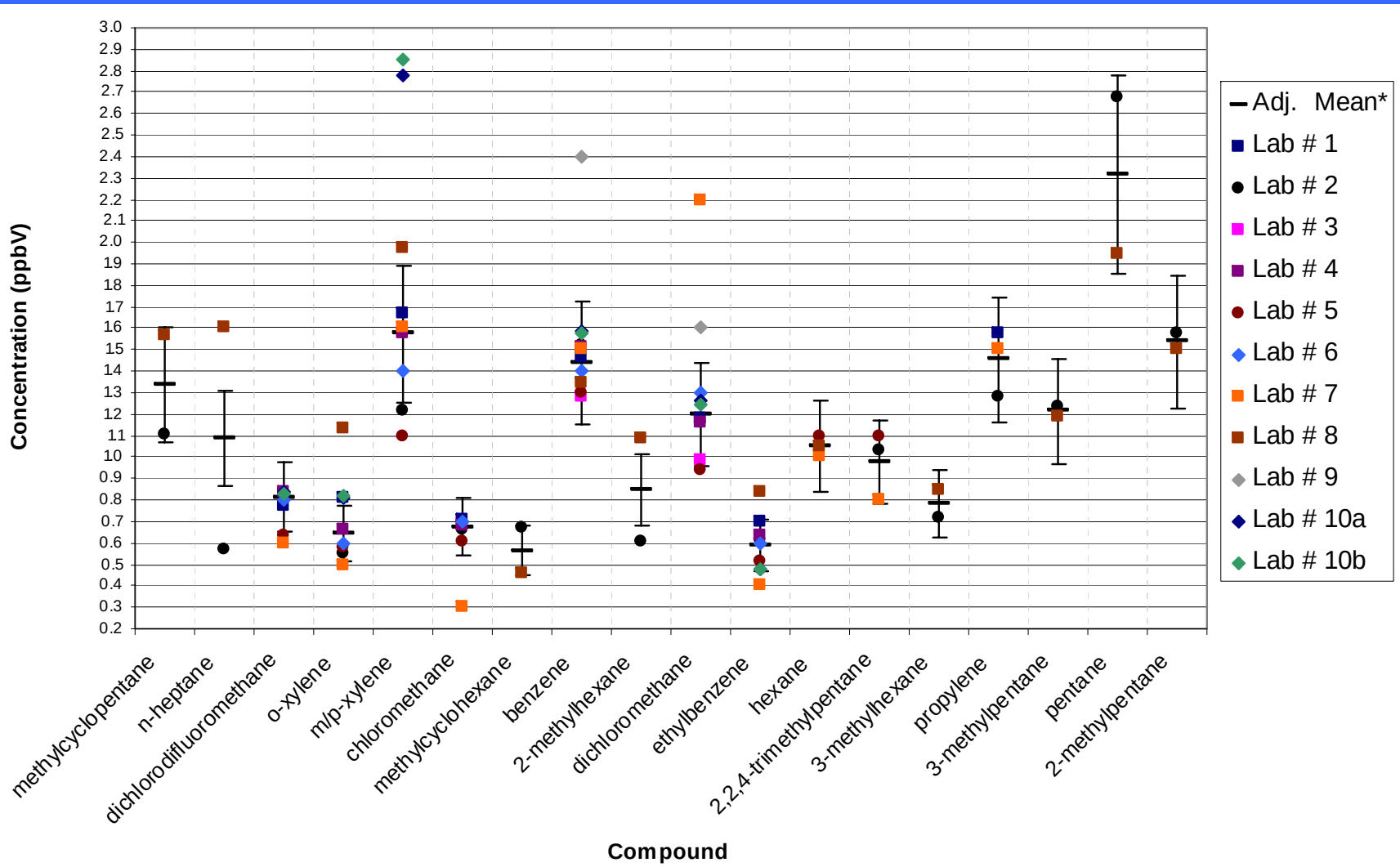
Compound	Lab 1a	Lab 1b	Lab 1 Avg	Lab 2a	Lab 2b	Lab 2c	Lab 2d	Lab 2e	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Total	Mean	St Dev	Lower Critical Value	Upper Critical Value	Adj Mean	St Dev of Adj Mean	St Dev from Adj Mean	
																						-2 SD	+2 SD
trans-2-butene	0.10	0.10	0.10	ND	ND	0.50	0.20	0.10	0.13	0.14	0.51	0.16	ND	ND	1.84	0.23	0.17	0.01	0.45	0.14	0.04	0.06	0.21
cis-2-butene	0.20	0.10	0.20	ND	ND	ND	0.10	0.20	0.14	0.17	0.26	0.15	ND	ND	1.22	0.17	0.05	0.11	0.24	0.16	0.04	0.08	0.24
1-pentene	0.30	0.40	0.40	1.20	0.40	0.40	0.40	0.60	0.30	0.44	0.62	ND	ND	ND	4.76	0.53	0.27	0.18	0.88	0.45	0.11	0.23	0.66
m-diethylbenzene	0.20	0.20	0.20	1.00	1.00	0.30	0.40	0.50	0.42	0.29	0.33	0.22	ND	ND	4.66	0.47	0.30	0.09	0.84	0.33	0.10	0.13	0.54
trans-2-pentene	0.20	0.20	0.20	0.60	0.50	0.40	0.40	0.50	0.12	0.43	--	0.32	ND	ND	3.47	0.39	0.15	0.19	0.58	0.39	0.11	0.18	0.60
cis-2-pentene	0.20	0.20	0.20	0.20	0.20	0.40	0.20	0.20	0.21	0.22	--	0.16	ND	ND	1.99	0.22	0.07	0.13	0.31	0.20	0.02	0.16	0.23
isopropylbenzene	0.20	0.20	0.20	0.20	0.20	0.60	0.10	0.20	0.26	0.73	--	0.35	ND	ND	2.84	0.32	0.21	0.04	0.59	0.22	0.07	0.07	0.36
p-diethylbenzene	0.30	0.30	0.30	0.80	ND	0.10	0.20	0.70	0.37	--	0.63	0.44	ND	ND	3.54	0.44	0.25	0.12	0.76	0.44	0.19	0.05	0.83
n-propylbenzene	0.70	0.80	0.80	0.80	1.10	0.40	0.50	0.70	0.96	1.12	0.67	1.24	1.10	ND	9.39	0.85	0.27	0.50	1.20	0.86	0.22	0.42	1.30
1-butene	0.50	0.50	0.50	0.50	0.50	0.30	0.50	0.50	0.43	0.56	0.53	0.50	1.10	1.92	7.84	0.65	0.44	0.09	1.22	0.54	0.20	0.14	0.93
p-ethyltoluene	1.30	1.30	1.30	1.30	1.20	1.20	0.80	1.40	1.20	1.38	1.14	1.63	1.10	1.17	14.82	1.23	0.20	0.98	1.49	1.24	0.10	1.04	1.44
n-octane	1.40	1.40	1.40	1.80	1.80	1.50	1.00	1.60	1.63	1.21	1.50	1.30	1.20	ND	15.94	1.45	0.26	1.12	1.78	1.42	0.17	1.08	1.75
n-undecane	1.20	1.20	1.20	1.10	1.40	0.60	0.80	1.80	1.21	1.47	1.93	1.55	1.50	2.04	16.60	1.38	0.43	0.83	1.94	1.46	0.28	0.91	2.01
2-methylheptane	1.10	1.20	1.20	1.50	1.40	1.00	1.00	1.30	1.32	1.49	0.95	1.28	1.20	0.92	14.56	1.21	0.21	0.95	1.48	1.18	0.16	0.86	1.51
3-methylheptane	0.90	0.80	0.90	1.10	0.90	1.30	0.80	1.10	1.13	1.15	0.86	1.04	1.10	ND	11.38	1.03	0.15	0.84	1.23	1.03	0.11	0.81	1.26
cyclopentane	1.10	1.10	1.10	1.30	1.10	1.00	1.10	1.20	0.74	1.21	1.06	1.07	1.10	0.78	12.76	1.06	0.16	0.85	1.27	1.10	0.07	0.97	1.24
n-nonane	1.50	1.50	1.50	1.50	1.60	1.30	1.10	--	1.47	1.61	1.20	1.75	1.50	1.35	15.88	1.44	0.19	1.20	1.69	1.45	0.14	1.17	1.72
o-ethyltoluene	0.90	0.90	0.90	0.90	1.00	0.80	0.80	1.20	1.14	0.95	0.77	1.82	1.30	ND	11.58	1.05	0.31	0.66	1.45	0.98	0.18	0.61	1.34
3,5-trimethylbenzer	1.00	1.00	1.00	1.10	0.90	0.90	0.50	0.80	0.96	1.69	0.89	0.77	1.20	ND	10.71	0.97	0.30	0.59	1.36	0.95	0.14	0.67	1.22
2,3-trimethylbenzer	0.80	0.80	0.80	1.10	0.60	0.90	0.70	1.30	2.56	1.03	3.02	0.56	1.10	ND	13.67	1.24	0.80	0.21	2.27	0.90	0.25	0.39	1.41
isoprene	0.90	0.90	0.90	2.10	1.60	1.40	1.20	1.60	0.60	1.04	0.90	1.14	ND	0.83	13.31	1.21	0.43	0.66	1.76	1.18	0.30	0.59	1.77
n-decane	1.60	1.70	1.70	1.50	1.80	1.40	1.40	1.50	2.92	1.73	1.70	--	1.90	2.15	19.70	1.79	0.44	1.23	2.35	1.68	0.24	1.20	2.15
m-ethyltoluene	1.80	1.90	1.90	2.20	2.00	1.60	1.80	1.70	2.02	2.53	2.16	3.32	2.30	2.03	25.56	2.13	0.45	1.55	2.71	2.02	0.27	1.48	2.56
2,4-trimethylbenzer	2.80	2.90	2.90	2.90	3.00	2.90	2.50	2.50	3.67	4.93	2.70	4.77	3.30	2.70	29.07	2.91	0.36	2.45	3.37	2.82	0.25	2.31	3.33
propylene	3.00	3.00	3.00	3.20	3.40	3.40	3.20	3.10	2.85	3.43	3.33	3.46	2.80	2.54	37.71	3.14	0.29	2.77	3.52	3.20	0.23	2.73	3.67
2,4-dimethylpentane	2.00	2.10	2.10	2.20	2.20	2.10	1.80	2.10	1.99	2.10	1.98	2.15	1.90	1.40	24.02	2.00	0.22	1.71	2.29	2.06	0.13	1.80	2.31
2,2-dimethylbutane	1.80	1.80	1.80	2.40	2.00	1.10	2.00	1.90	1.25	2.04	1.83	2.10	1.60	1.20	21.22	1.77	0.40	1.25	2.28	1.84	0.27	1.30	2.37
n-heptane	2.30	2.30	2.30	2.80	2.50	2.60	1.90	2.40	2.42	2.80	2.33	2.69	2.60	2.07	29.41	2.45	0.28	2.10	2.80	2.54	0.18	2.18	2.91
3,4,-trimethylpentar	1.80	1.80	1.80	2.20	2.10	2.50	1.70	1.90	2.02	2.20	1.96	2.21	2.50	1.84	24.93	2.08	0.26	1.75	2.41	2.03	0.16	1.70	2.35
cyclohexane	2.20	2.20	2.20	2.60	2.90	2.20	1.80	2.90	2.15	2.37	2.20	2.22	2.00	1.53	27.07	2.26	0.40	1.74	2.77	2.19	0.22	1.75	2.64
ethylbenzene	2.40	2.40	2.40	3.00	2.70	2.10	1.90	2.40	2.46	2.68	2.42	3.16	2.60	2.36	30.18	2.52	0.35	2.07	2.96	2.46	0.19	2.09	2.83

Producing the Report

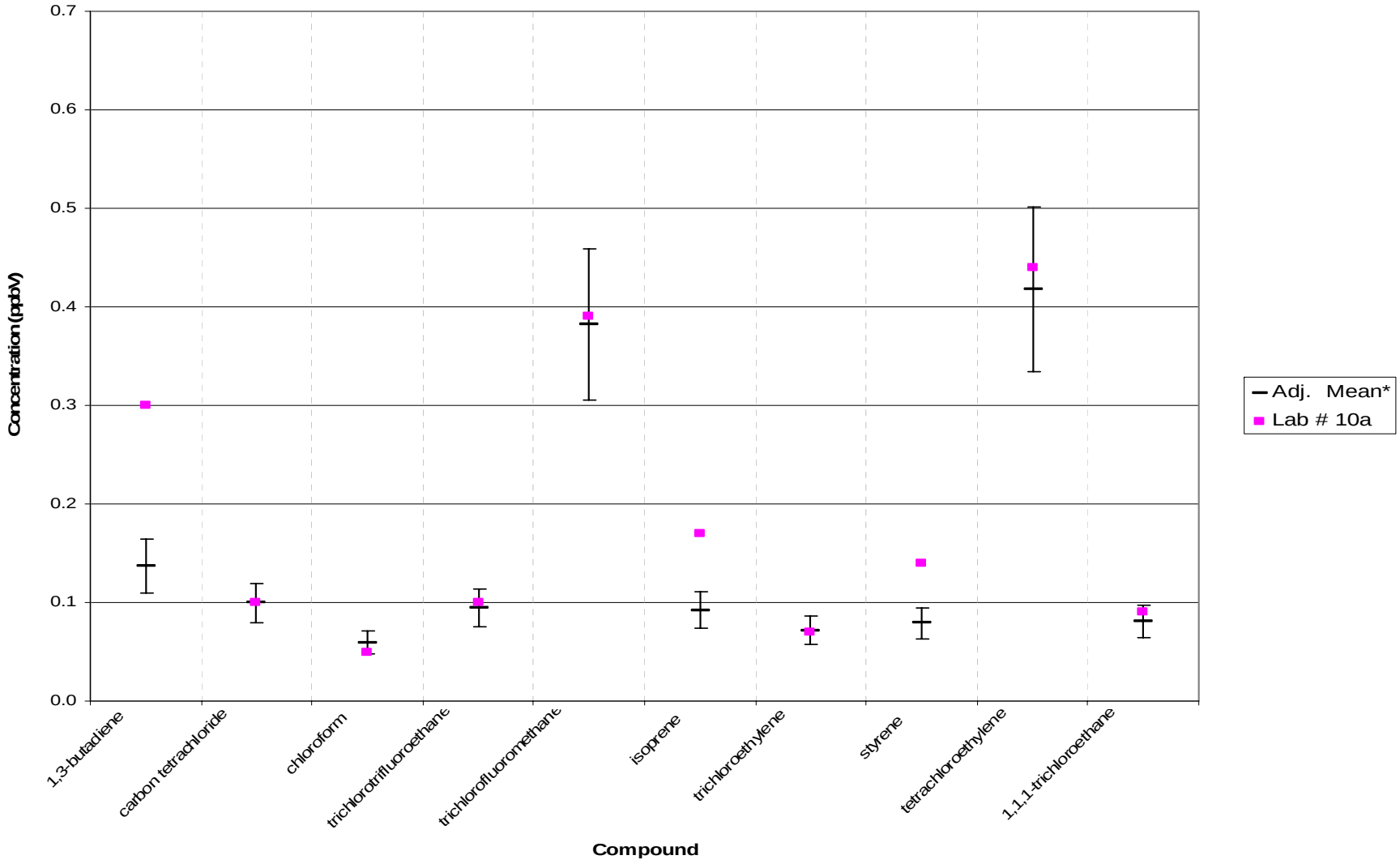
- Graphs are formed comparing all laboratory responses against the adjusted mean and standard deviation response.

- Each laboratory is notified of its performance, comparing their individual response to the adjusted mean response, for each of the compounds it had reported.

Multiple Lab Comparison Graphs



Single Lab Comparison Graphs



Web-based Information

- Hydrocarbon species
  - www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/whole/wholetable.htm
- Toxics species
  - www.arb.ca.gov/aaqm/qmosqual/perfaudit/toxics/whole/wholetable.htm
- Program contact
  - Charles Pearson cpearson@arb.ca.gov

Conclusion

- The Ambient Air Interlaboratory Comparisons have steadily progressed since its inception.
- Future improvements may include :
  - Expanding samplers capability
  - Introduction of tracer compound
  - Develop a comparison for Carbonyls
  - Investigate different statistical techniques