IMPROVING CONFIDENCE IN THE TO-15 ATMOSPHERIC ANALYSIS AT TRACE CONCENTRATIONS

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Canister Cleaning and meaningful low concentration results; a cold harsh reality

Disclaimer

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There is no endorsement of any products mentioned or shown in this presentation. They are presented for methodology information only.

Why is this talk different than a TO-15 Method Talk and why do we need trace levels?

- Many TO-15 analysis have high reporting limits.
  - 100 pptv and higher.
  - Risk based target concentrations can be extremely low << 50 pptv.
- Modeling typically uses ½ the detection level as a value overestimating many compounds.
- National Air Toxics Trends Study (NATTS) is targeting lower concentrations in their program.
- Achieve ambient air concentrations.

http://www.epa.gov/superfund/sites/npl/hrsaddition.htm#visl

	µg/m3	pptv
1,1,2,2-tetrachlorethane	0.048	7
tetrachloroethene	1.11	162
trichloroethene	0.48	89
1,1,2-trichlorothane	0.18	33
vinyl chloride	0.17	67
1,2-dibromoethane	0.0047	1
benzyl chloride	0.057	11
benzene	0.36	100
acrolein	0.021	9

Indoor Vapor Intrusion Calculator*

*There are no uncertainties listed in these target values, personal communication with risk assessor stated 3 orders of magnitude!

Ambient Air Health Comparison Values

Compound	CAS	Risk-based health comparison values for chronic exposures (lowest value shaded orange)		
		1-in-1-million cancer risk, ppt	10-in-1-million cancer risk, ppt	Noncancer effects, ppb
acrolein	107-02-8	n/a	n/a	0.009
napthalene; 45850	91-20-3	5.6	56	0.57
propylene dichloride	78-87-5	11	114	0.87
1,3-butadiene	106-99-0	15	151	0.90
acrylonitrile	107-13-1	6.8	68	0.92
ethylene dibromide	106-93-4	0.22	2.2	1.2
methyl bromide	74-83-9	n/a	n/a	1.3
benzene	71-43-2	39	393	9.2
carbon tetrachloride	56-23-5	26	265	16
chloroform	67-66-3	n/a	n/a	20
xylenes	1330-20-7	n/a	n/a	23
vinyl chloride	75-01-4	44	437	38
1,4-dichlorobenzene	106-46-7	15	152	133
hexane	110-54-3	n/a	n/a	198
ethylbenzene	100-41-4	92	922	230
methyl chloroform	71-55-6	n/a	n/a	926
toluene	108-88-3	n/a	n/a	1326
1,1,2,2-tetrachloroethane	79-34-5	2.5	25	n/a
ethylene dichloride	107-06-2	9.5	95	n/a
tetrachloroethylene	127-18-4	25	250	n/a
trichloroethylene	79-01-6	93	931	n/a
methylene chloride	75-09-2	608	6079	n/a

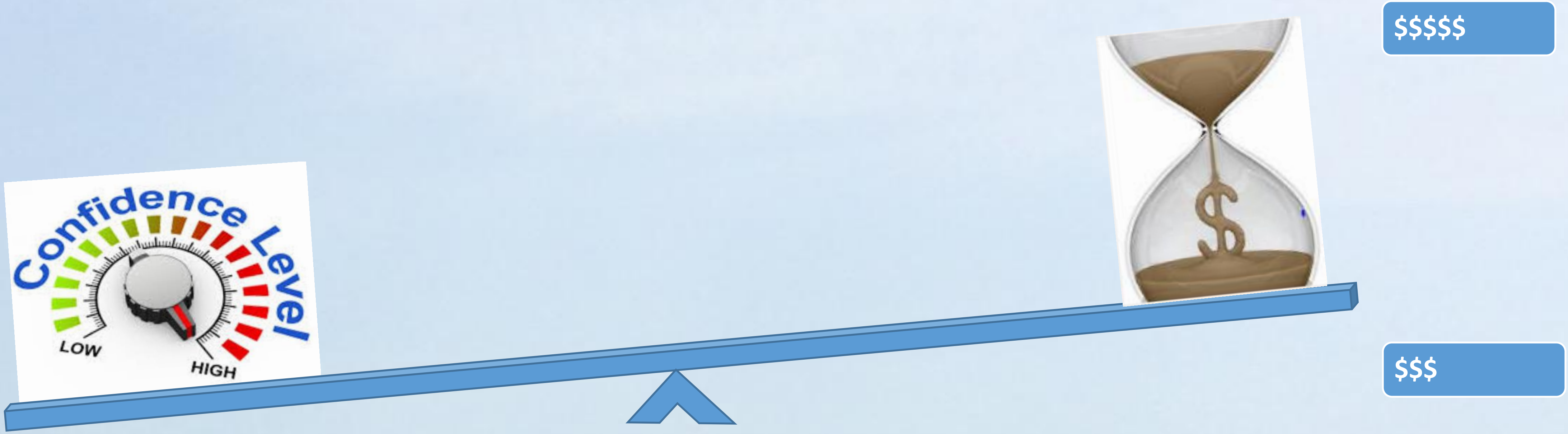
Concentrations are derived from the cancer Unit Risk Estimates (UREs) from IRIS and other sources

NATTS Draft TAD

HAP	10^{-6} Cancer Risk Concentration (µg/m³)	Noncancer Risk [Hazard Quotient = 0.1] Concentration (µg/m³)
acrolein	-	0.002
tetrachloroethylene	3.8462 [2]	4 [2]
Benzene (**41 pptv**)	0.13	3
carbon tetrachloride (**27 pptv**)	0.17	19
trichloroethylene	0.2083 [2]	0.2 [2]
1,3-butadiene	0.03	0.2
vinyl chloride	0.11	10
Acrylonitrile (**7 pptv**)	0.015	2
bromoform	0.91	-
carbon disulfide	-	70
chloroprene	-	0.7
p-dichlorobenzene (**15 pptv**)	0.091	80
cis-1,3-dichloropropene	0.3	2
trans-1,3-dichloropropene	0.3	2
ethyl acrylate	0.071	-
hexachloro-1,3-butadiene (**.02 pptv**)	0.0022	9
methyl tert-butyl ether	3.8	300
methylene chloride	2.1	100
1,1,2,2-tetrachloroethane (**0.3 pptv**)	0.017	-
1,1,2-trichloroethane	0.063	40
formaldehyde	0.08 [2]	0.08 [2]
acetaldehyde	0.45	0.9

Achieving these limits with ~~high~~ any confidence

- The achieve these low limits most laboratories and project planners will have to balance added **confidence in the results** against the **expense and time** of the rigorous procedures to obtain the confidence.



What are the limiting factors for ultra trace concentrations?

- Instrument limitations (single quadrupole full scan or selective ion monitoring (SIM), Time of Flight (TOF))
- Background in makeup and carrier gasses, He, N_2, Zero Air
- Cleanliness and integrity in:
  - regulators and standard makeup (including internal standards and surrogates if added)
  - sample preparation, preconcentrator
  - <u>canisters or alternative containers</u>
  - sample train (passive regulators, connections, transfer lines, pumps)
- Accuracy of calibration procedures
- Carry over in instrument
  - Naphthalene and other compounds with high vapor pressures

What solutions are used to engineer out, minimize or deal with contamination interferences?

- Dedicated and clean regulators for standards
  - internal standard, 1 ppmv standard, varying analytes
- <u>A more rigorous canister cleaning procedure</u>
- <u>Certify each canister and not by batch</u>
  - selective batch certification as next best approach
  - match certification selection results to sample results
- Calibrate using a linear or quadratic force through zero curve fit when possible and a % error acceptance criteria at each calibration level
- Check integrity of canisters with low concentration spikes
  - not routinely performed at CRL
- If an environmental chamber is available, use zero air to test regulators and sample train, right now CRL uses lab air

Avoid SIM unless very confident from interferences

- Often 1,3-butadiene may be mostly n-butane secondary ion, no unique ion between them
- Acrolein can be product of nmhc secondary ions.
- Other interferences possible and can only be sure in full scan mode
- Interferences are not in standards or performance testing samples.

Terms for reporting data

Calibration Range- Area from reporting limit to upper calibration standard concentration, +/- 50% @ RL, 30% above

Reporting Limit- Lowest reporting value acceptable from curve that meets +/- 50 % with all levels above +/- 30%

Detection Level- Lowest concentration analyzed that has a signal to noise of 5 or greater.

concentration chosen by ability to make a reliable standard and data quality objectives

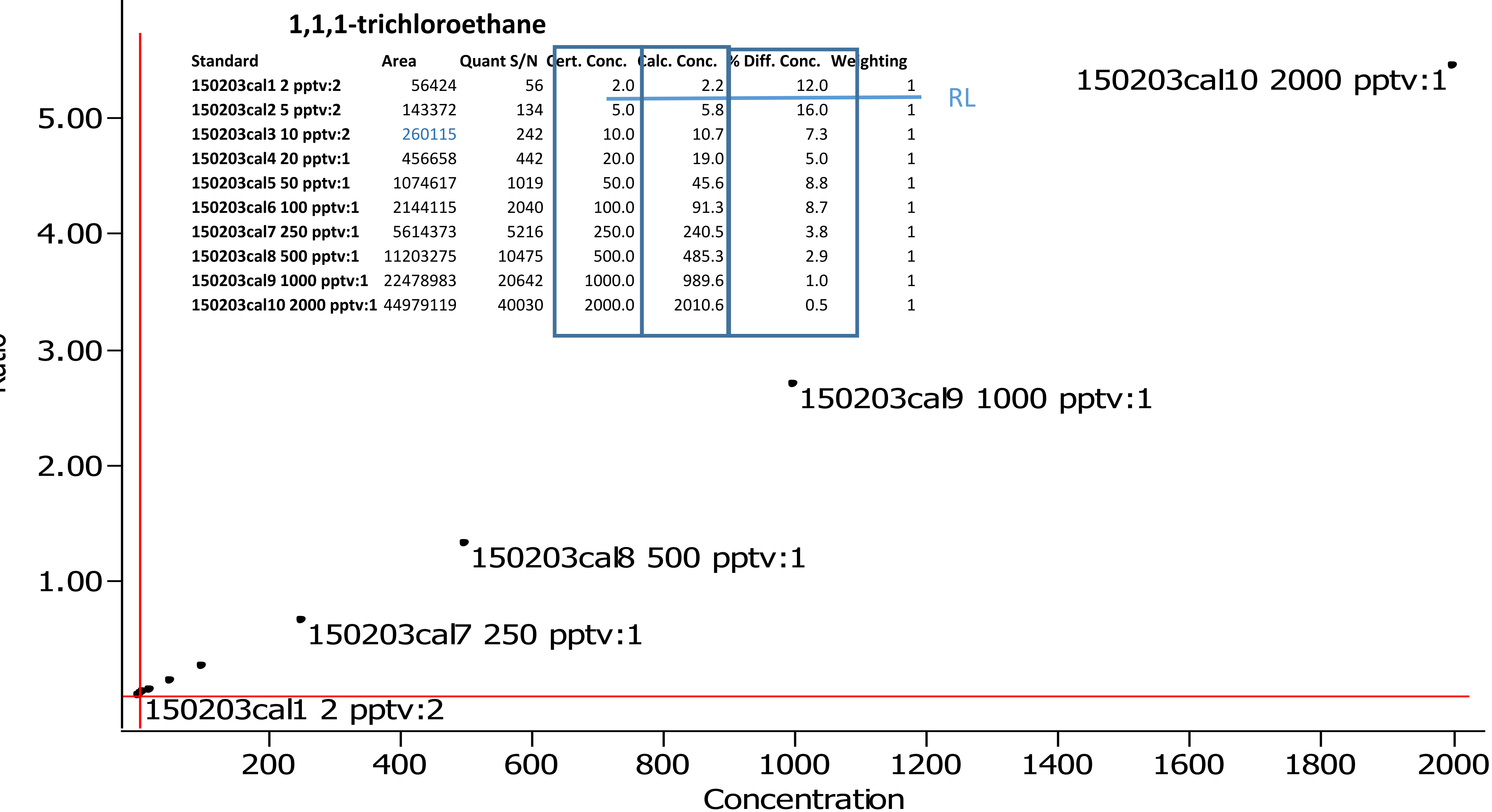
Calibration Curve Fits

- Use linear or quadratic
- Force through zero whenever possible
  - Makes it easy to see the interferences are present
  - Greatly improves accuracy at low concentrations
- Weight calibration curve when not forcing through zero
- Check with % error between expected and calculated from calibration curve
  - ± 50 % error at RL, ± 30 % all points above,
  - Most levels should be tighter to about ± 10%
- Never, ever, never report below a non-force through zero calibration level using a quadratic curve! WJW 27 Oct 2015

1,1,1-trichloroethane

Standard	Area	Quant S/N	Cert. Conc.	Calc. Conc.	% Diff. Conc.	Weighting
150203cal1 2 pptv:2	56424	56	2.0	2.2	12.0	1
150203cal2 5 pptv:2	143372	134	5.0	5.8	16.0	1
150203cal3 10 pptv:2	260115	242	10.0	10.7	7.3	1
150203cal4 20 pptv:1	456658	442	20.0	19.0	5.0	1
150203cal5 50 pptv:1	1074617	1019	50.0	45.6	8.8	1
150203cal6 100 pptv:1	2144115	2040	100.0	91.3	8.7	1
150203cal7 250 pptv:1	5614373	5216	250.0	240.5	3.8	1
150203cal8 500 pptv:1	11203275	10475	500.0	485.3	2.9	1
150203cal9 1000 pptv:1	22478983	20642	1000.0	989.6	1.0	1
150203cal10 2000 pptv:1	44979119	40030	2000.0	2010.6	0.5	1

RL



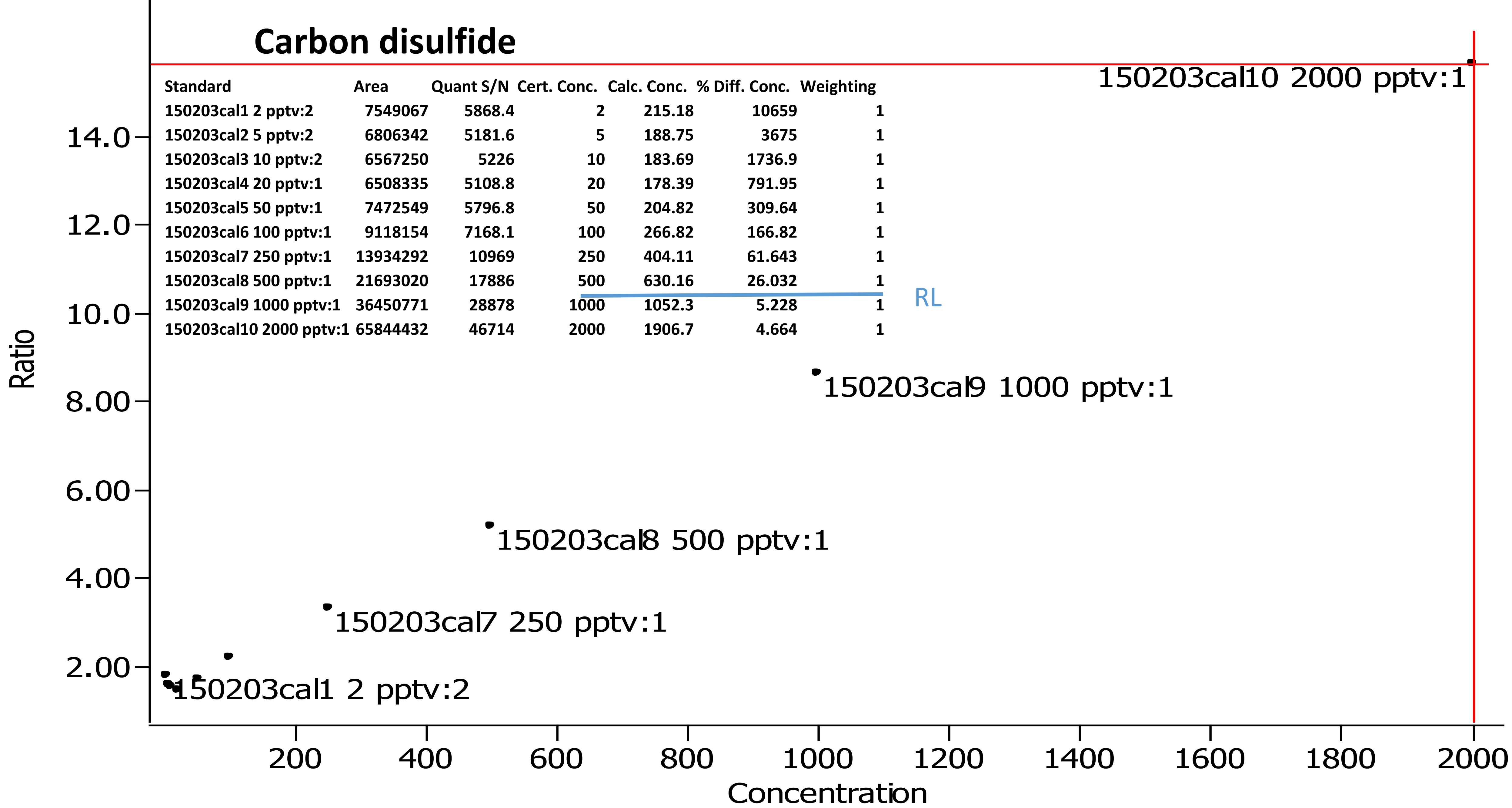
y= +0.00271438x + 0
r = 0.99994

Forced zero intercept

Carbon disulfide

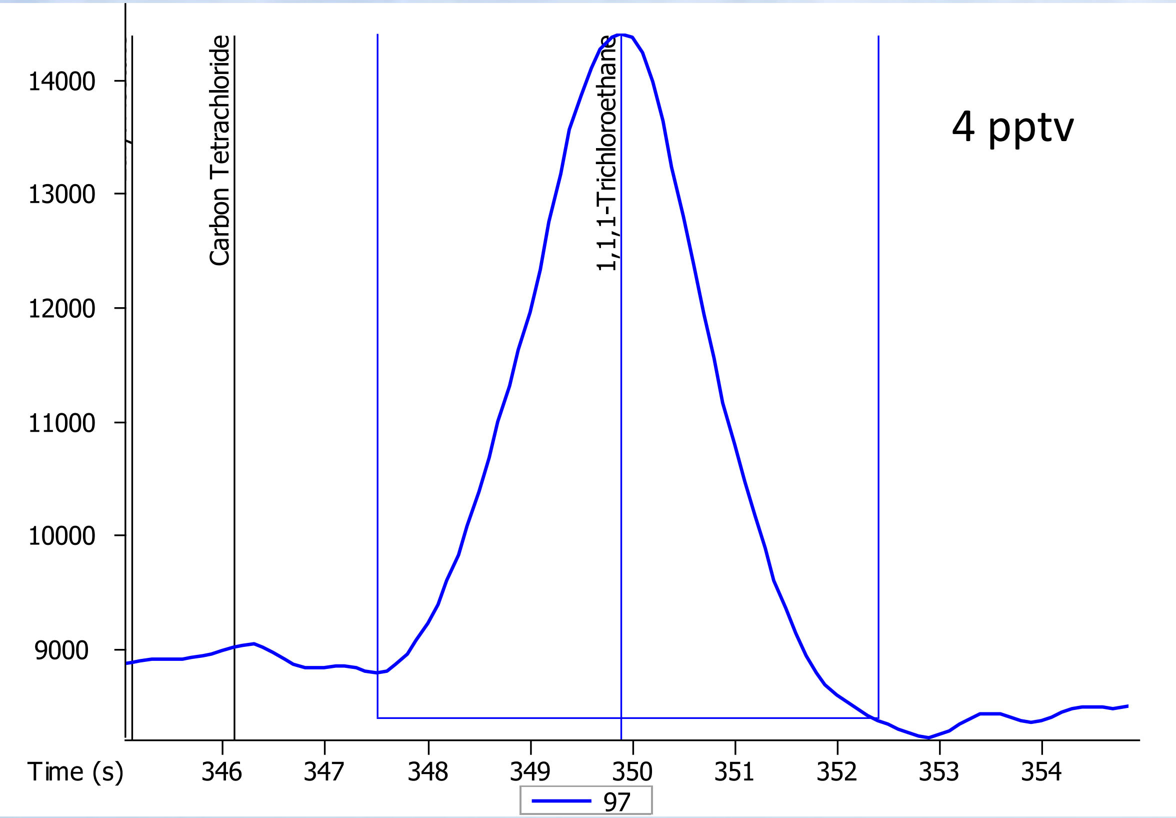
Standard	Area	Quant S/N	Cert. Conc.	Calc. Conc.	% Diff. Conc.	Weighting
150203cal1 2 pptv:2	7549067	5868.4	2	215.18	10659	1
150203cal2 5 pptv:2	6806342	5181.6	5	188.75	3675	1
150203cal3 10 pptv:2	6567250	5226	10	183.69	1736.9	1
150203cal4 20 pptv:1	6508335	5108.8	20	178.39	791.95	1
150203cal5 50 pptv:1	7472549	5796.8	50	204.82	309.64	1
150203cal6 100 pptv:1	9118154	7168.1	100	266.82	166.82	1
150203cal7 250 pptv:1	13934292	10969	250	404.11	61.643	1
150203cal8 500 pptv:1	21693020	17886	500	630.16	26.032	1
150203cal9 1000 pptv:1	36450771	28878	1000	1052.3	5.228	1
150203cal10 2000 pptv:1	65844432	46714	2000	1906.7	4.664	1

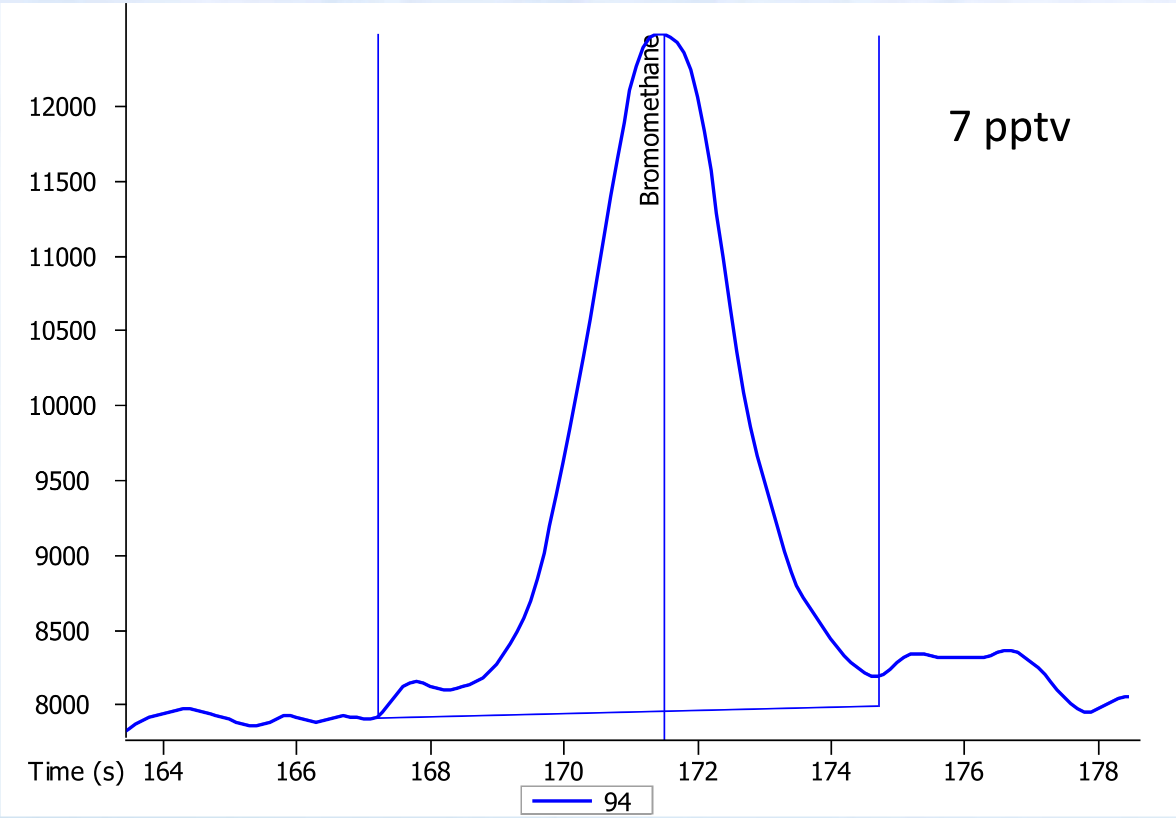
RL



y= +0.00821202x + 0
r = 0.99960

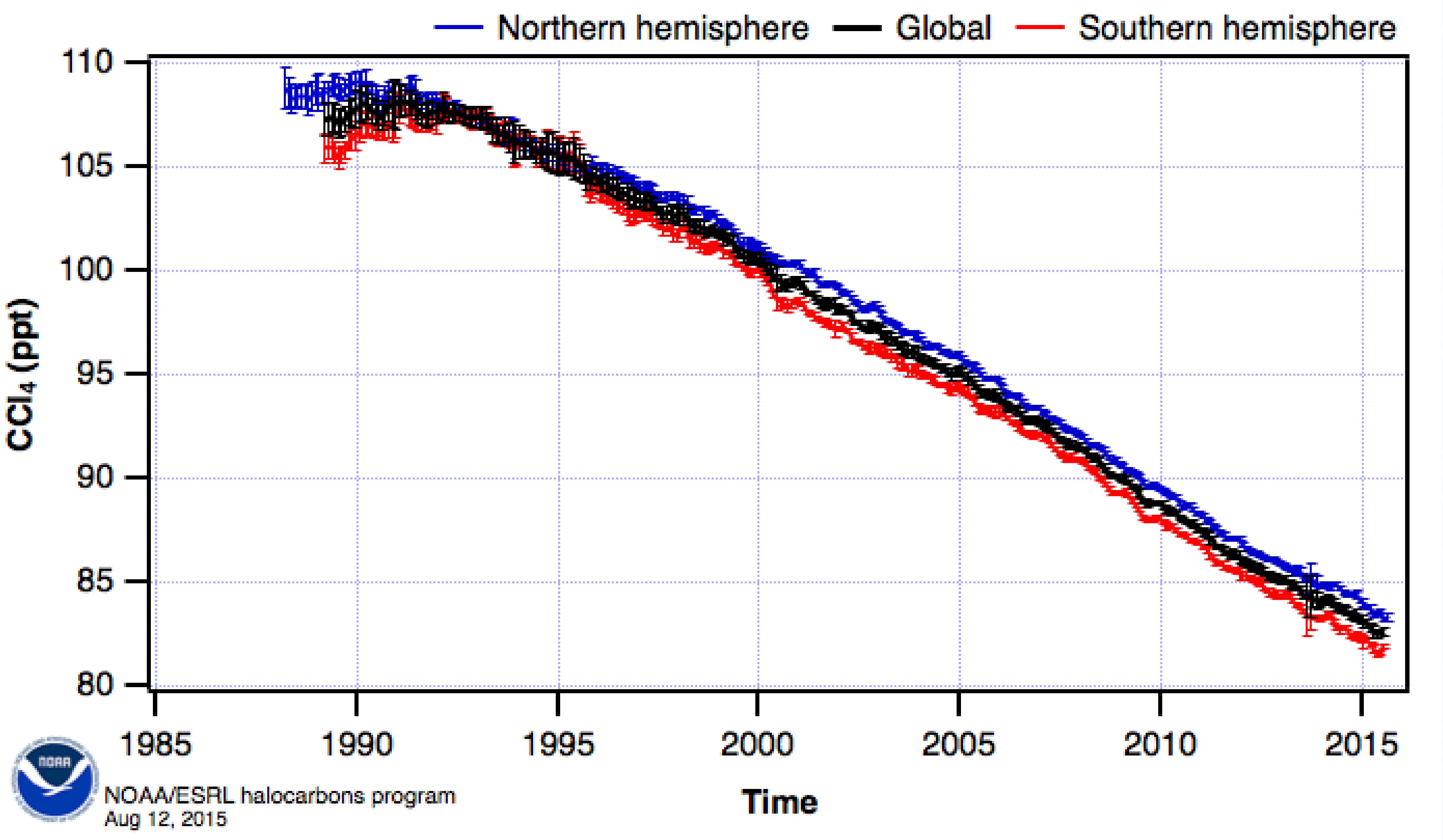
Two compounds that are in every ambient air sample at very low concentrations

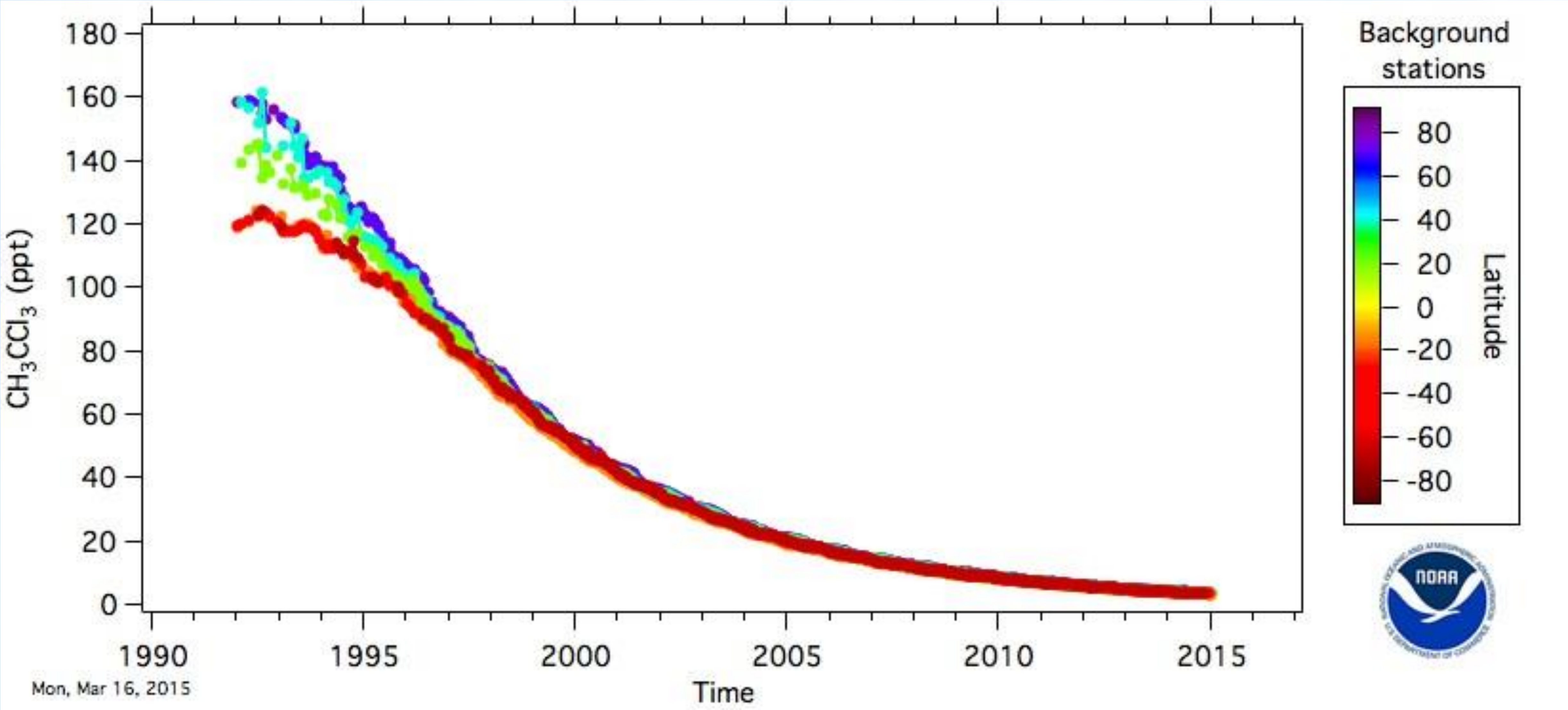




200 mL air sample

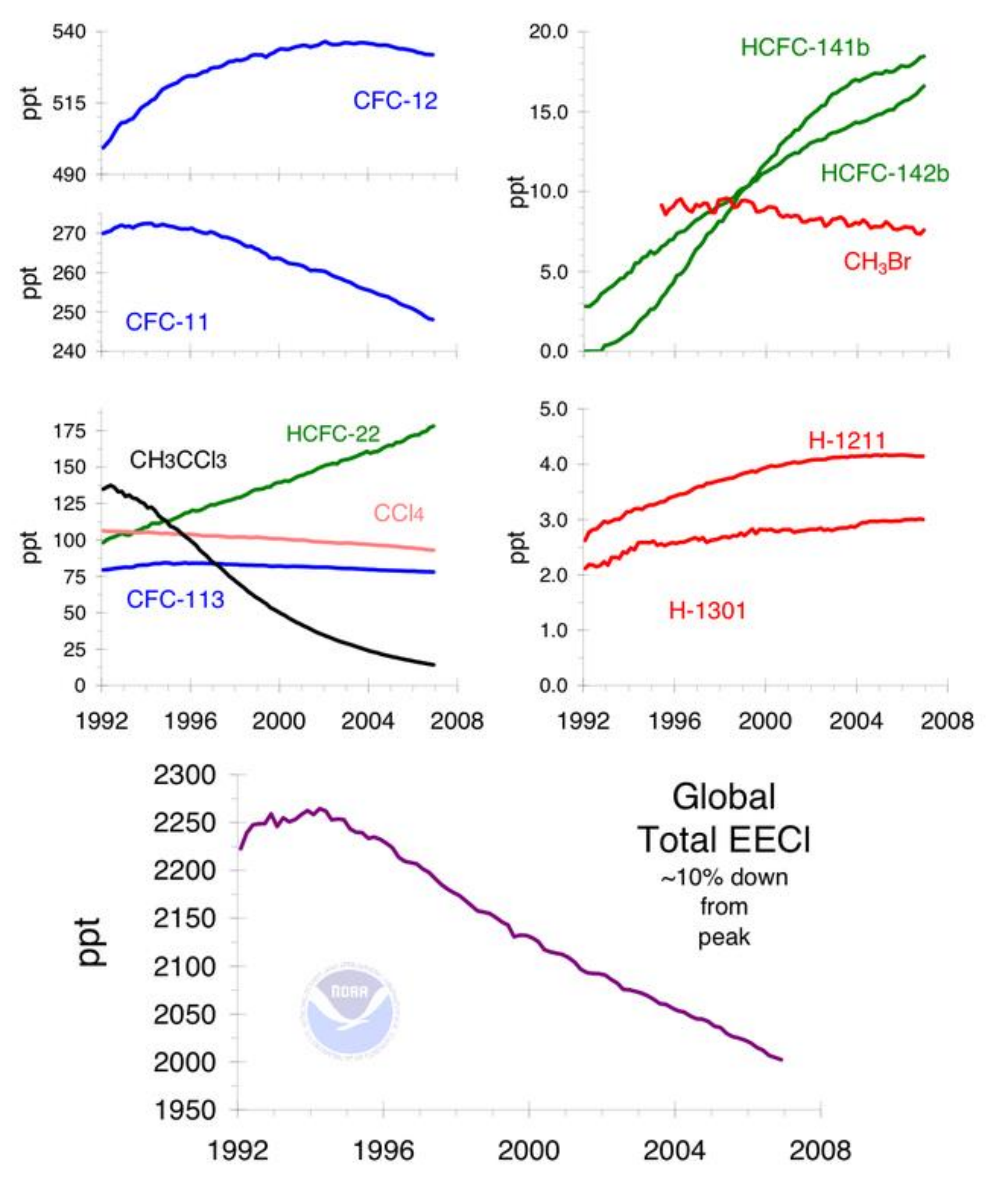
Reality Check



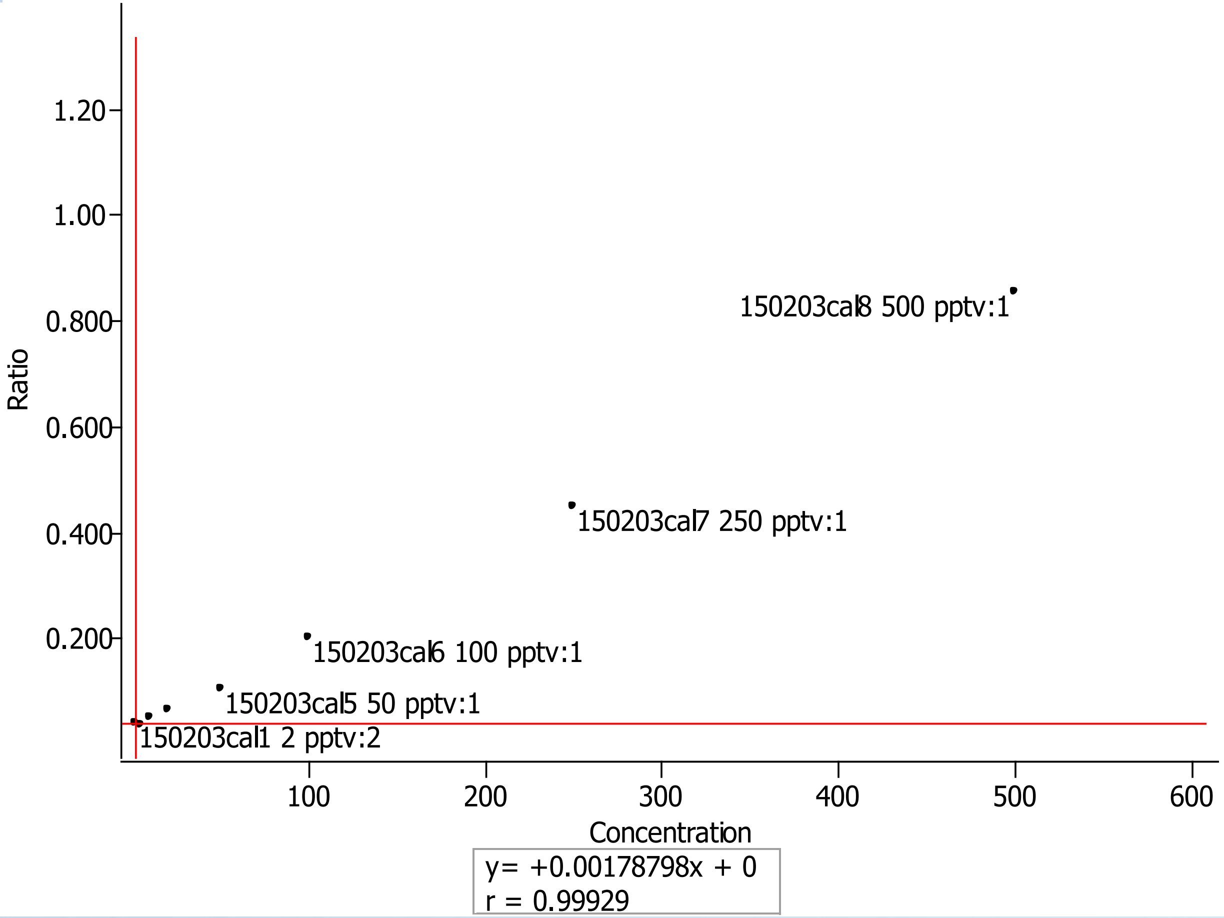


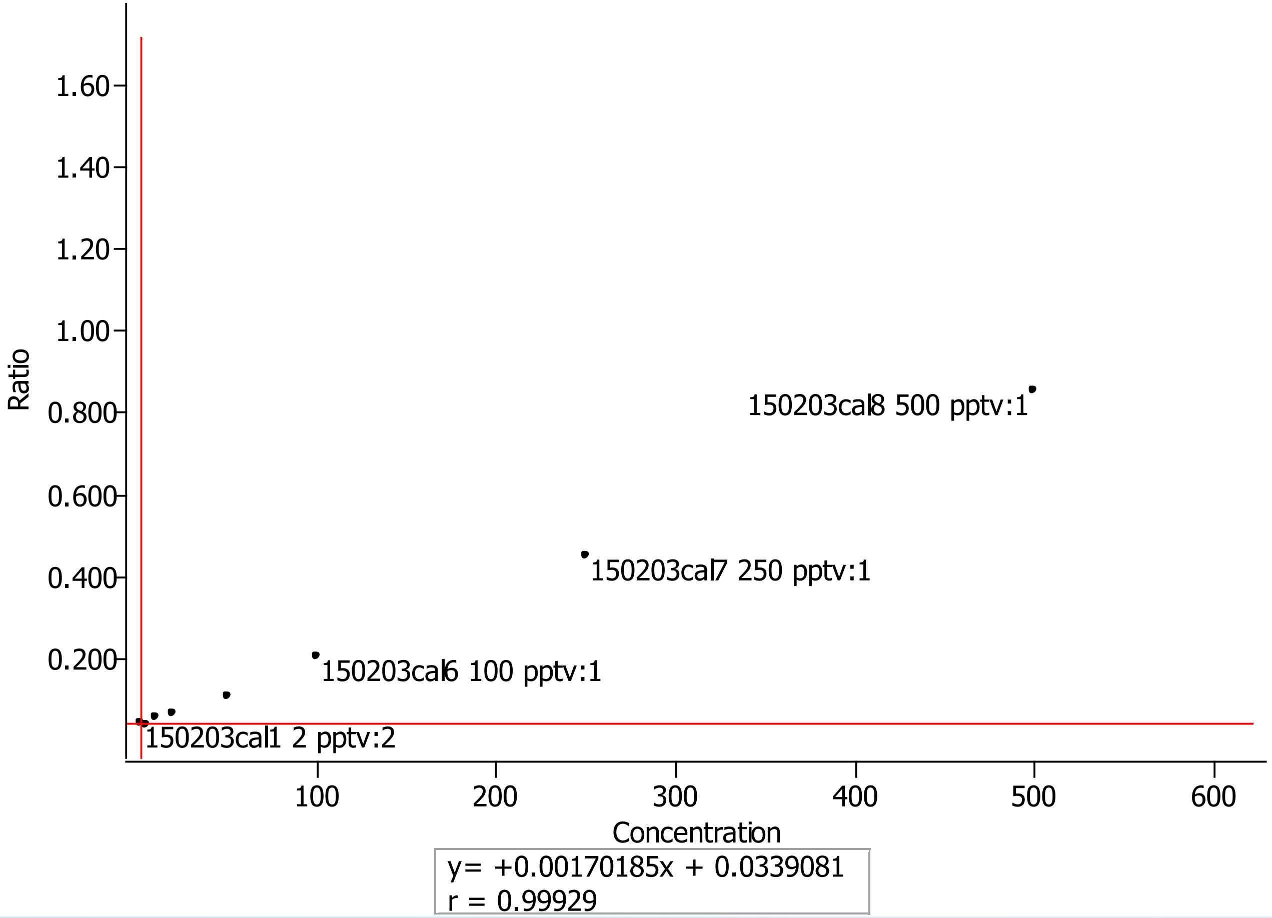
CH_3CCl_3 (ppt)
180
160
140
120
100
80
60
40
20
0
1990
1995
2000
2005
2010
2015
Time
Mon, Mar 16, 2015
Background stations
80
60
40
20
0
-20
-40
-60
-80
Latitude

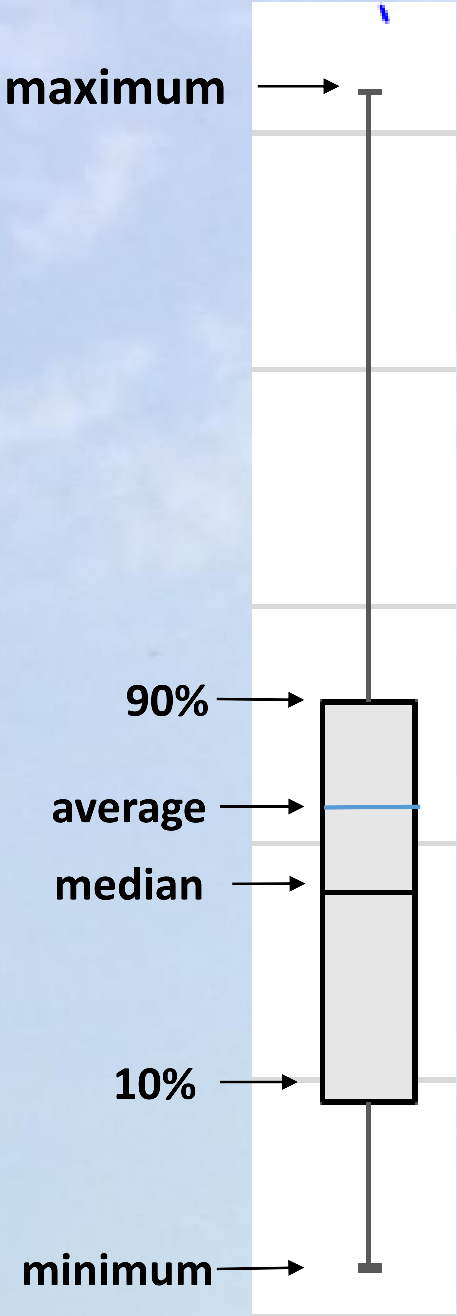
Halocarbon Global Trends



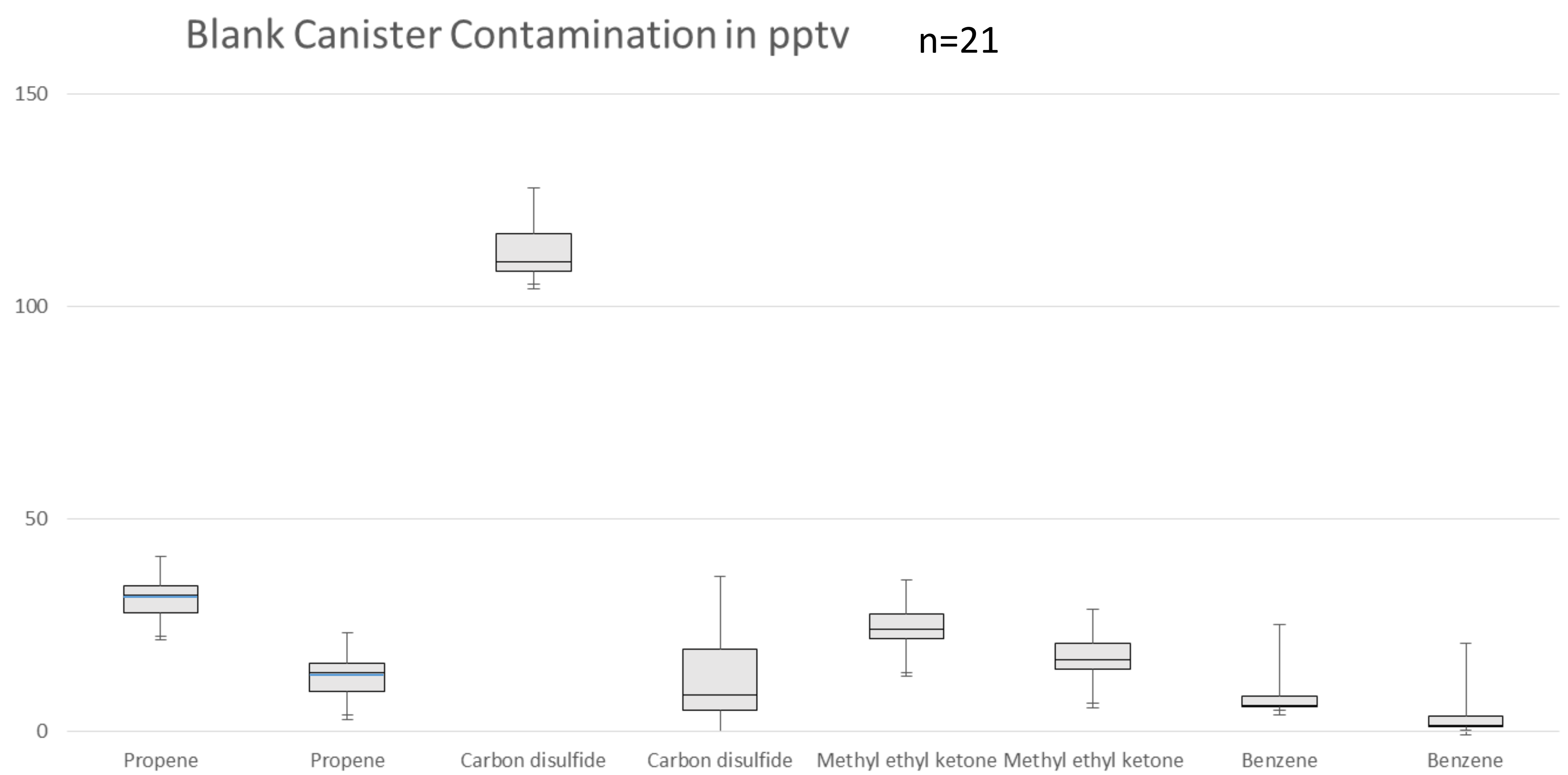
Propene Calibration Curves w and w/o forced zero







Box and Whisker Plot Legend
For blank canister data



n=21

Propene calibration

Force Zero | Calculated Intercept

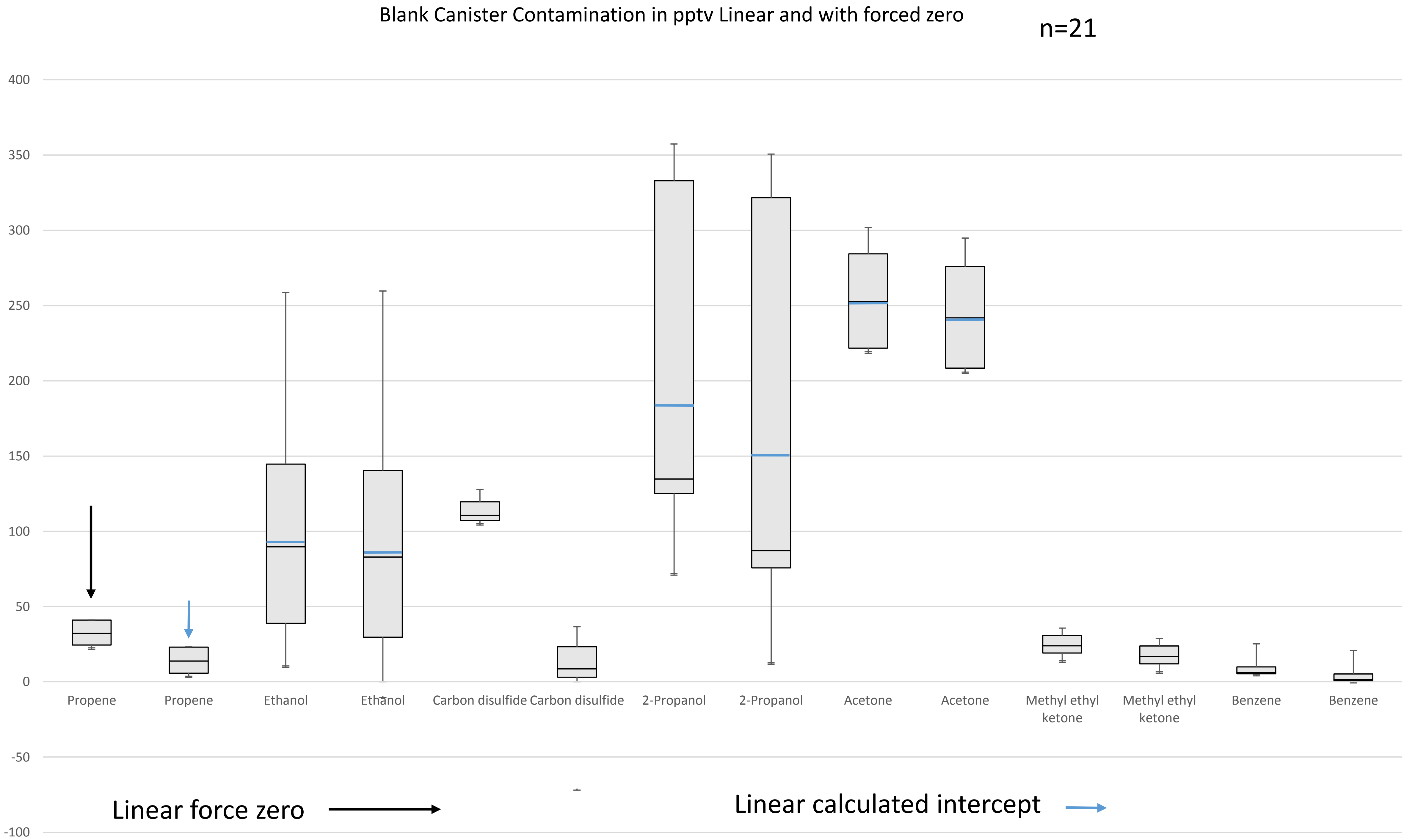
Standard	Area	Quant S/N	Cert. Conc.	Calc. Conc.	% Diff. Conc.	Weighting	Calc. Conc.	% Diff. Conc.
150203cal1 2 pptv:2	168794	54.629	2	22.1	1005	0.5	3	65
150203cal2 5 pptv:2	169726	59.511	5	21.6	332	0.2	3	44
150203cal3 10 pptv:2	229931	76.979	10	29.5	195	0.1	11	11
150203cal4 20 pptv:1	287833	100.74	20	36.2	81	0.05	18	9
150203cal5 50 pptv:1	467081	154.08	50	58.8	18	0.02	42	16
150203cal6 100 pptv:1	842995	266.54	100	113.3	13	0.01	99	1
150203cal7 250 pptv:1	1880888	590.75	250	250.5	0	0.004	243	3
150203cal8 500 pptv:1	3583291	1062	500	478.1	4	0.002	482	4
150203cal9 1000 pptv:1	7245002	1983	1000	960.6	4	0.001	989	1
150203cal10 2000 pptv:1	14783116	3743.9	2000	1966.2	2	0.0005	2046	2

RL (Force Zero): below 150203cal5 50 pptv:1

RL (Calculated Intercept): below 150203cal2 5 pptv:2

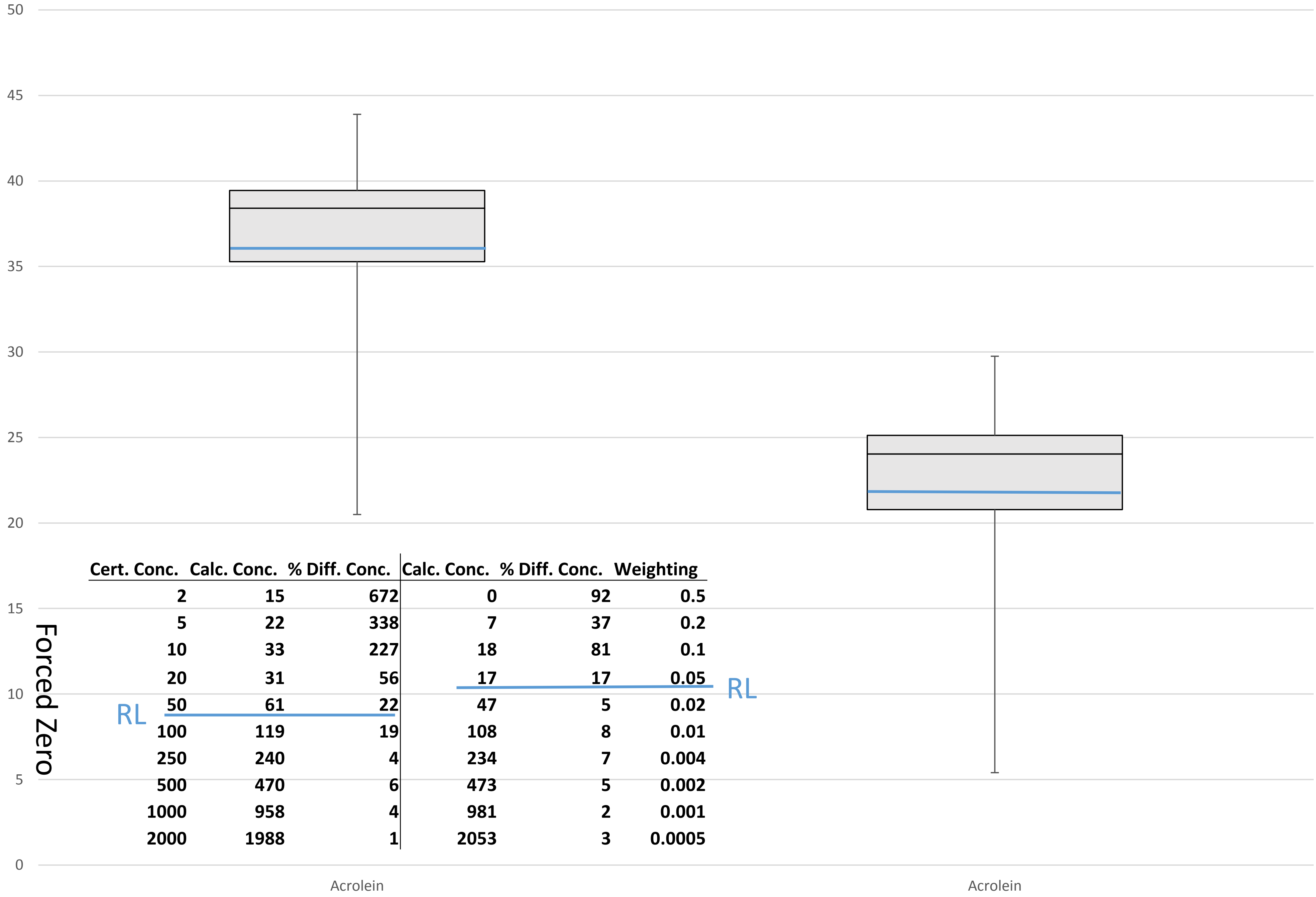
-50

-100


Blank Canister Contamination in pptv Linear and with forced zero
n=21
400
350
300
250
200
150
100
50
0
-50
-100
Propene
Propene
Ethanol
Ethanol
Carbon disulfide
Carbon disulfide
2-Propanol
2-Propanol
Acetone
Acetone
Methyl ethyl ketone
Methyl ethyl ketone
Benzene
Benzene
Linear force zero
Linear calculated intercept

Blank Contamination Linear Fit W and W/O Force 0

n=19



Forced Zero

Cert. Conc.	Calc. Conc.	% Diff. Conc.	Calc. Conc.	% Diff. Conc.	Weighting
2	15	672	0	92	0.5
5	22	338	7	37	0.2
10	33	227	18	81	0.1
20	31	56	17	17	0.05
50	61	22	47	5	0.02
100	119	19	108	8	0.01
250	240	4	234	7	0.004
500	470	6	473	5	0.002
1000	958	4	981	2	0.001
2000	1988	1	2053	3	0.0005

RL

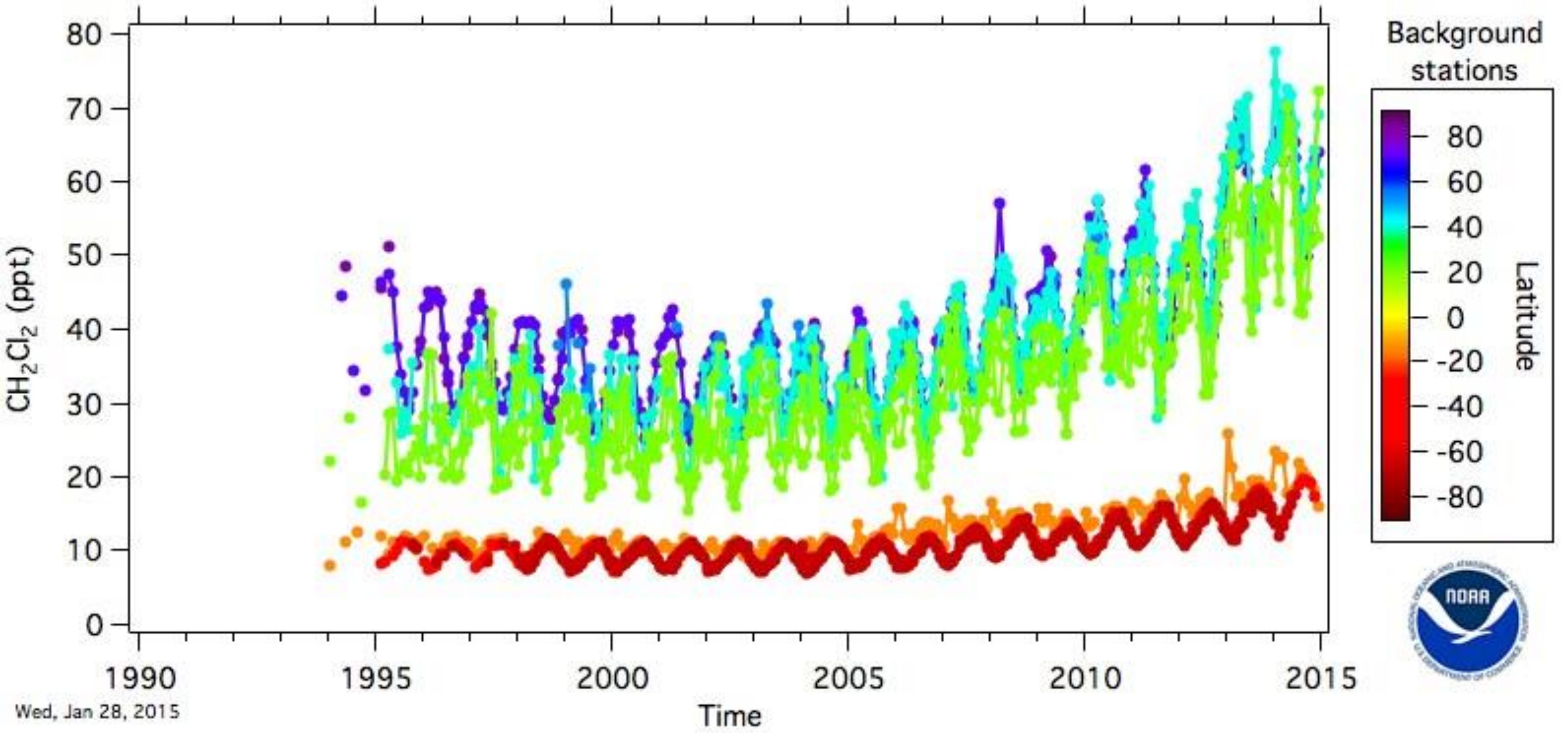
RL

Results of Freons with Various Curve Fits

cal name	Quantification pptv	Sample	expected	% difference	pptv	Sample	expected	% difference
141028 CFC average RF	1,1,1-Trichloroethane	3.33	4	17%	Carbon Tetrachloride	61.7	83	26%
141028 CFC lin 0 1W	1,1,1-Trichloroethane	4.05	4	-1%	Carbon Tetrachloride	71.1	83	14%
141028 CFC lin 0 invW	1,1,1-Trichloroethane	4.01	4	0%	Carbon Tetrachloride	70.2	83	15%
141028 CFC linear	1,1,1-Trichloroethane	-2.62	4	166%	Carbon Tetrachloride	62.6	83	25%
141028 CFC linear invW	1,1,1-Trichloroethane	-1.81	4	145%	Carbon Tetrachloride	64.6	83	22%
141028 CFC average RF	1,1,2-Trichloro-1,2,2-Trifluoroethane	61.3	72	15%	Dichlorodifluoromethane	348	510	32%
141028 CFC lin 0 1W	1,1,2-Trichloro-1,2,2-Trifluoroethane	74.6	72	-4%	Dichlorodifluoromethane	423	510	17%
141028 CFC lin 0 invW	1,1,2-Trichloro-1,2,2-Trifluoroethane	72.5	72	-1%	Dichlorodifluoromethane	407	510	20%
141028 CFC linear	1,1,2-Trichloro-1,2,2-Trifluoroethane	53.6	72	26%	Dichlorodifluoromethane	401	510	21%
141028 CFC linear invW	1,1,2-Trichloro-1,2,2-Trifluoroethane	61.6	72	14%	Dichlorodifluoromethane	405	510	21%
141028 CFC average RF	Dichlorotetrafluoroethane	19.7	20	2%	Trichlorofluromethane	171.0	235	27%
141028 CFC lin 0 1W	Dichlorotetrafluoroethane	19.7	20	2%	Trichlorofluromethane	192.4	235	18%
141028 CFC lin 0 invW	Dichlorotetrafluoroethane	19.8	20	1%	Trichlorofluromethane	190.6	235	19%
141028 CFC linear	Dichlorotetrafluoroethane	19.7	20	2%	Trichlorofluromethane	185.5	235	21%
141028 CFC linear invW	Dichlorotetrafluoroethane	19.8	20	1%	Trichlorofluromethane	187.2	235	20%

RF =Response factor, lin 0 1W = linear forced 0 equally weighted, lin 0 invW = linear forced zero intercept 1/x weighted, linear = linear 1/x weighted calculated intercept, linear invW = linear calculated intercept 1/x weighted

Dichloromethane global temporal data and a sample set with two calibration methods



cal name	Sample Concentration
141028 CFC lin 0 1W	218
141028 CFC linear	98
141028 CFC lin 0 1W	218
141028 CFC linear	95
141028 CFC lin 0 1W	160
141028 CFC linear	68
141028 CFC lin 0 1W	159
141028 CFC linear	72
141028 CFC lin 0 1W	147
141028 CFC linear	66
141028 CFC lin 0 1W	161
141028 CFC linear	73

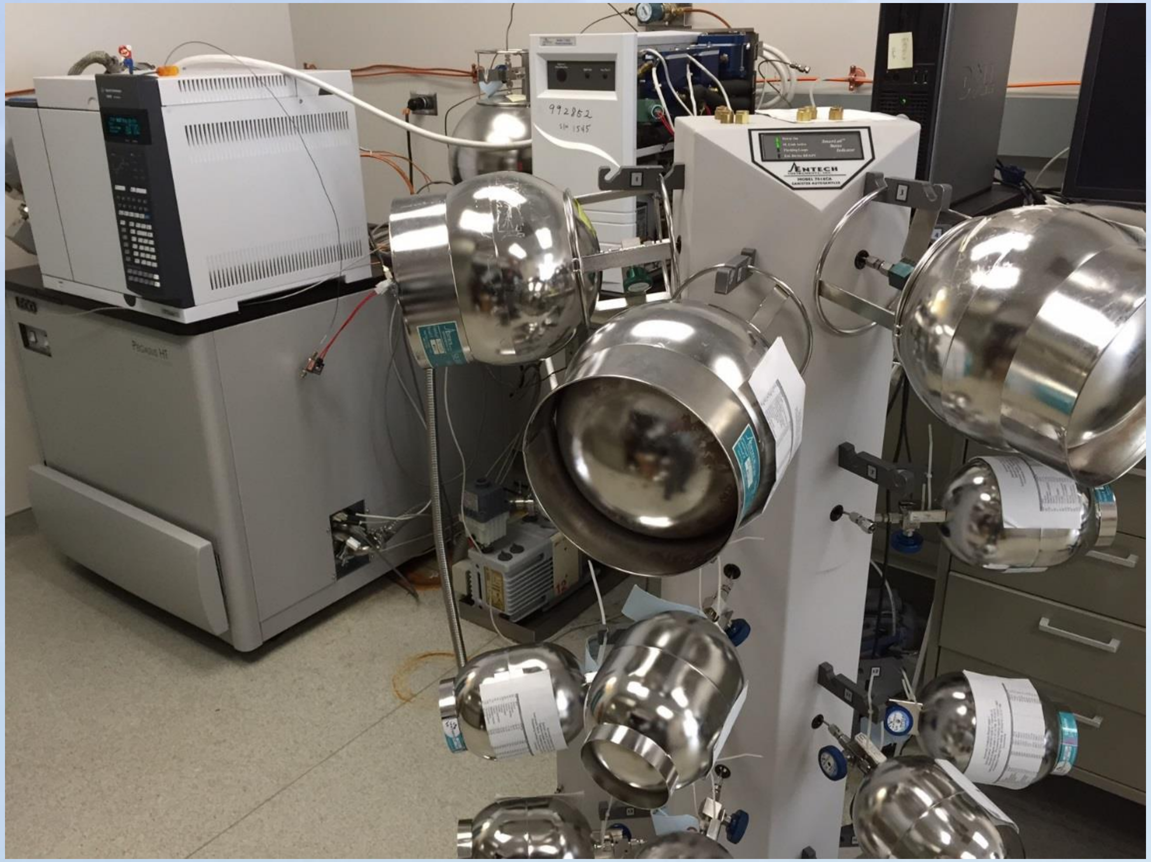
Data from one week at site in Indiana

Calibration based RL 50 pptv 0 int, <blank> $_{0int}$ = 18 pptv, n=20, <blanks > $_{linear}$ = 0.6 pptv n=20

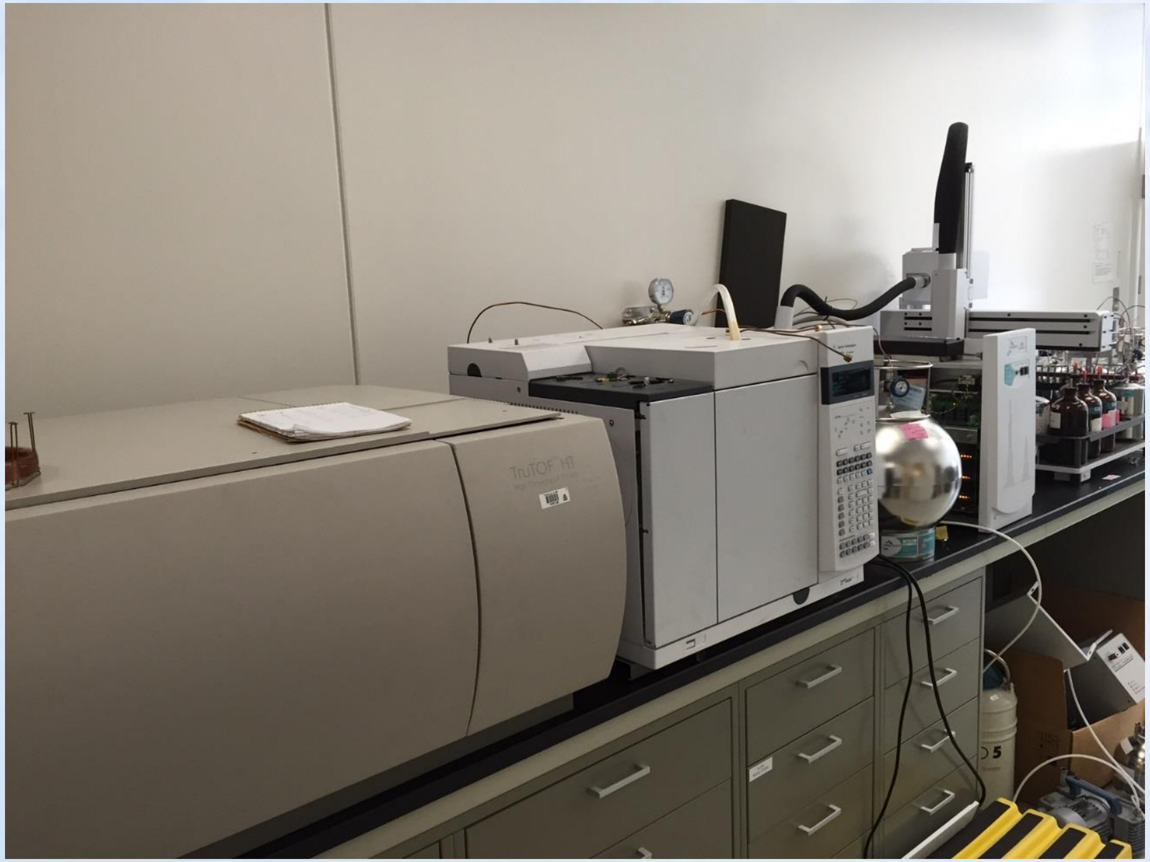
Using calibration force through zero vs. non force through zero

- Force through zero
  - Gives better results with very low concentration and extremely little background or inconsistent background.
  - Provides ability to understand background interferences.
  - May give false positives when not used properly and careful attention to contamination sources are not observed.
- Calculated intercept
  - Best used when a much more constant background is present.
  - May supply false negatives and negative concentrations.
  - Always best to engineer out interferences whenever possible.

Peggy cold trap dehydration Amelia



LECO Pegasus HT, Agilent 7890,
Entech 7100, Entech 7016
Most compounds 1 to 5 pg > 5 S/N FS



LECO TruTOF, Agilent 7890,
Entech 7200, Entech 7650
Most compounds 1 to 5 pg > 5 S/N FS

Canister Cleaning

90 ° C
vacuum to 50 mtorr
flush to 20 psi whole air
sit 2 minutes
repeat 10- 20 times

90 °C for 3 days open to room air
flush immediately with zero air

Canister Storage

Store canisters in zero air 20 psia
with quantitation report of blank cert.,
keep report with data file, and match to sample,
flag if detected in blank and canister > 5 times blank

Quantification	MAX pptv	average, pptv	count
2-Propanol	351	151	21
Acetone	295	242	21
Ethanol	250	79	21
Naphthalene	109	-27	20
trans-1,2-Dichloroethene	53	14	12
1,2,4-Trichlorobenzene	38	10	21
Ethyl Acetate	30		15
Acrolein	30	20	20
Methyl ethyl ketone	29	17	21
Tetrachloroethene	27	3	21
Propene	23	13	21
Dichlorodifluoromethane	22	12	18
Benzene	21	4	21
Benzyl chloride	15	5	13
1,2-Dichloroethane	14		4
1,4-Dichlorobenzene	12	4	21
2-Hexanone	12	10	8
Trichloroethene	11	4	17
trans-1,3-Dichloropropene	10	7	12
Hexachlorobutadiene	9	-1	21
1,3-Dichlorobenzene	9	2	21
1,2-Dibromoethane	8	3	17
Tetrahydrofuran	7		2
cis-1,3-Dichloropropene	7	5	9
1,2-Dichlorobenzene	7	1	19
Styrene	7	-6	21

[High]

[Low]

Canister Blank Data

20 x cycle cleaning

Other compounds under a max concentration of 5 pptv.

21 cans

Quantification	MAX, pptv	n	Average, pptv
Naphthalene	232	13	36
Acetone	84	17	30
Ethanol	83	6	34
1,2,4-Trichlorobenzene	54	13	25
1,3-Dichlorobenzene	37	15	4
Methyl ethyl ketone	19	16	7
2-Propanol	18	17	6
Benzyl chloride	17	1	
Acrolein	16	10	13
1,4-Dioxane	15	15	0
Propene	12	17	-1
Methylene Chloride	12	17	5
1,2-Dichlorobenzene	11	17	2
2-Hexanone	9	6	4
Benzene	9	16	4
Hexachlorobutadiene	9	17	3
Toluene	9	17	2
1,2,4-Trimethylbenzene	8	11	2
1,4-Dichlorobenzene	8	10	2
Dichlorodifluoromethane	7	11	2

Canister Blank Data

3 day oven cleaning

Other compounds under a max concentration of 5 pptv.

17 cans some from soil gas

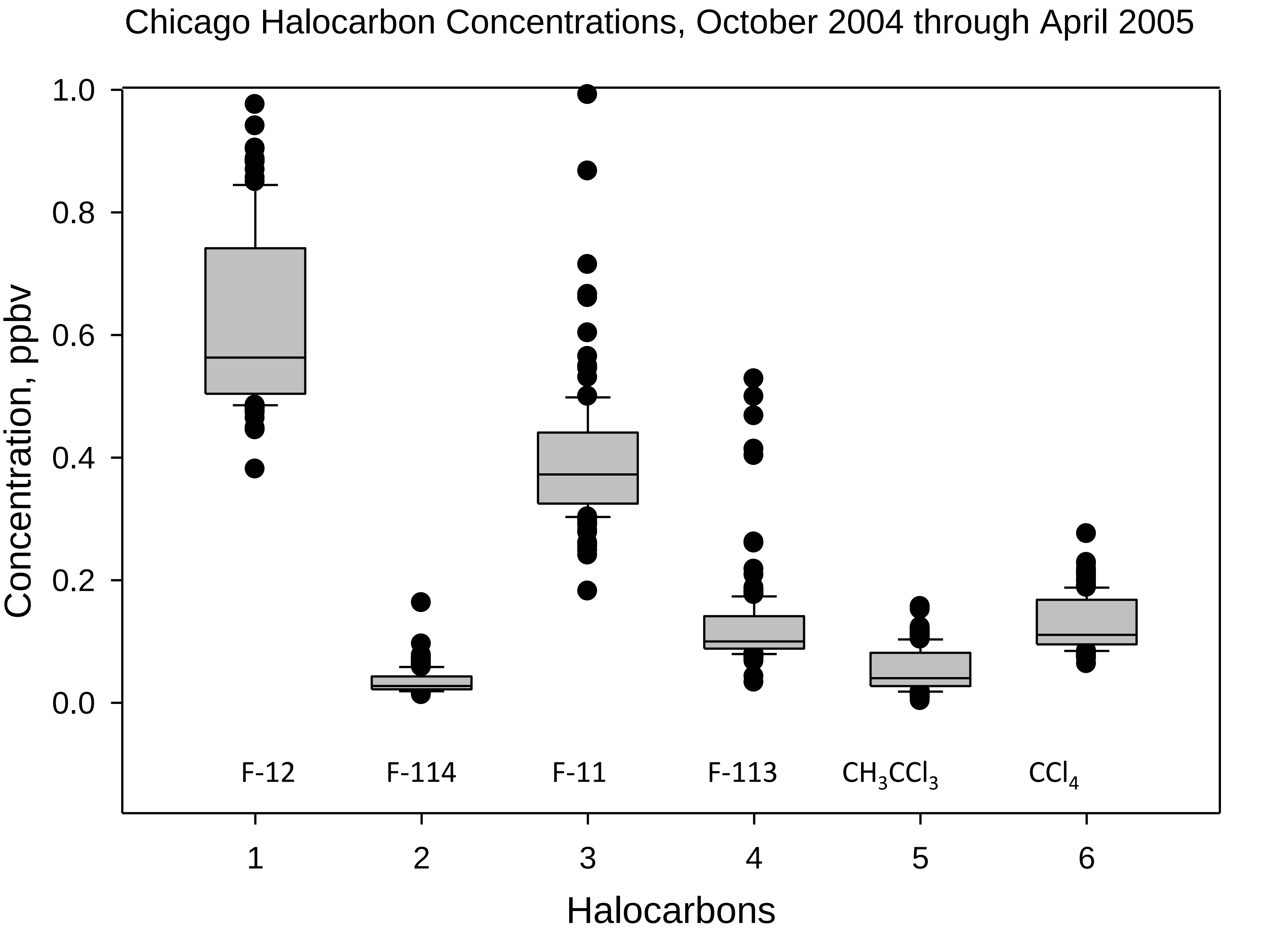
How to clean, and test sampling trains?
Quality of sample is only as good as the weakest link in the sample path

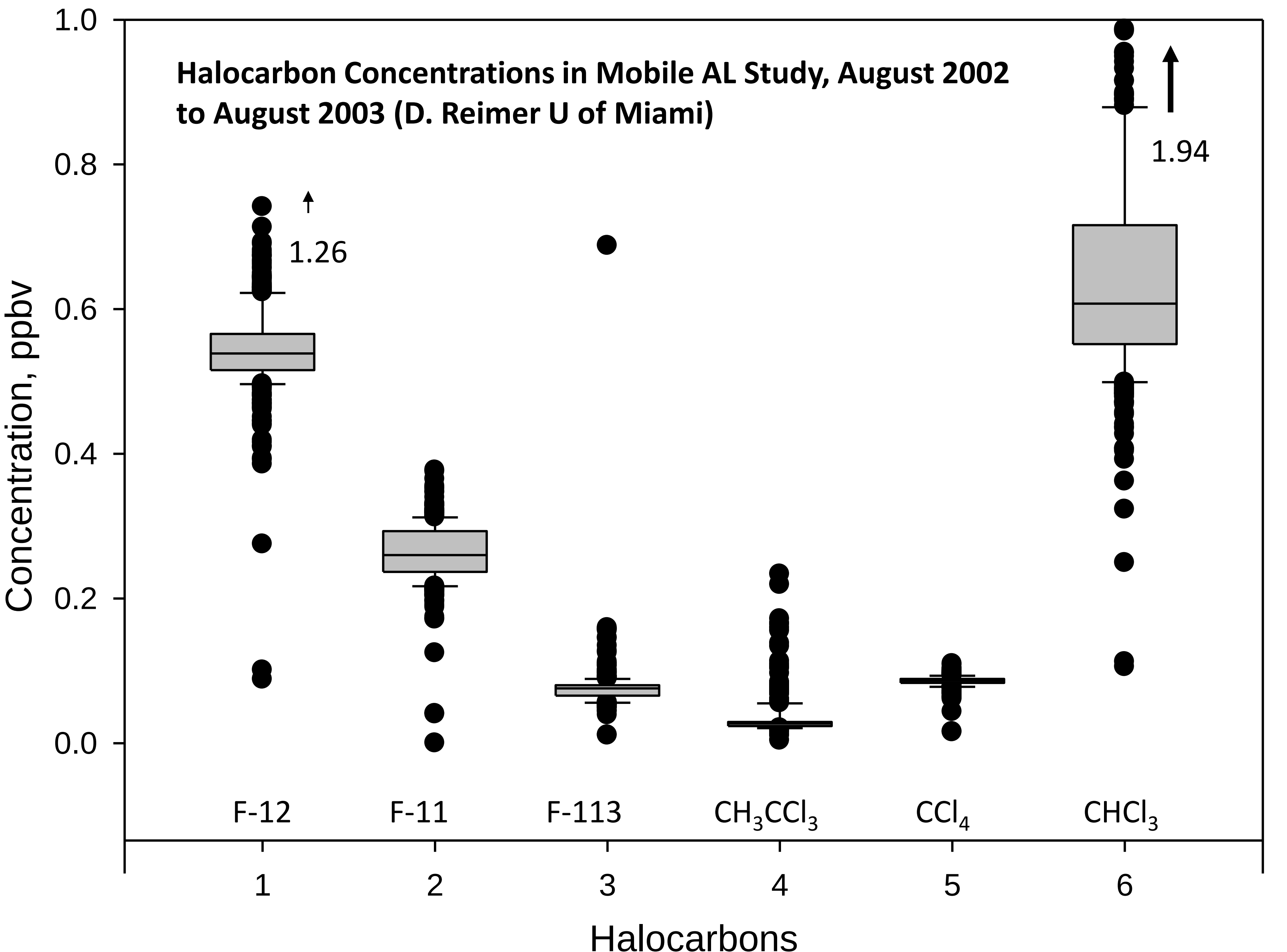
Picture from Entech Instrument Catalogue

Canister Integrity?

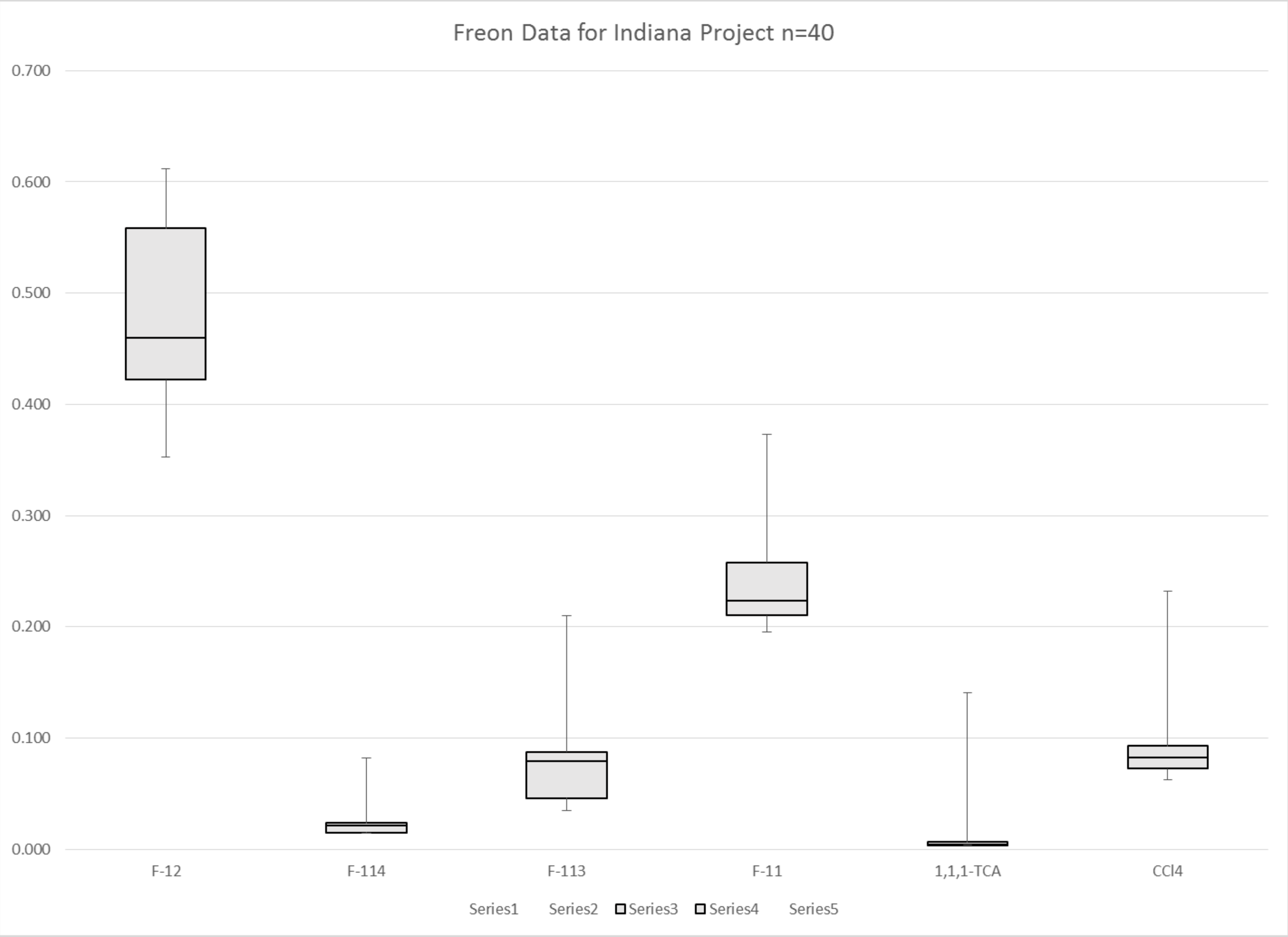
- One lab rigorously cleaned new canisters delivered to lab and tested each with zero air.
  - Compounds still present in one canister, vinyl chloride, benzene and acrolein at 100 pptv or less
- Filled canisters with 500 pptv and elevated acrolein and depressed 1,3-butadiene and dichloropropenes.

2002 Chicago Study for Freons as Surrogates


Chicago Halocarbon Concentrations, October 2004 through April 2005
1.0
0.8
0.6
0.4
0.2
0.0
Concentration, ppbv
F-12
F-114
F-11
F-113
CH3CCl3
CCl4
1
2
3
4
5
6
Halocarbons



Halocarbon Concentrations in Mobile AL Study, August 2002 to August 2003 (D. Reimer U of Miami)
Concentration, ppbv
0.0
0.2
0.4
0.6
0.8
1.0
1.26
1.94
F-12
F-11
F-113
CH3CCl3
CCl4
CHCl3
1
2
3
4
5
6
Halocarbons


Freon Data for Indiana Project n=40
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
F-12
F-114
F-113
F-11
1,1,1-TCA
CCl4
Series1
Series2
Series3
Series4
Series5

Sample Monitoring Compounds (Freons) Data Over 2 Month Sampling Mission

pptv	1,1,1-TCA	F-11	CCl4	F-12	F-113	F-114
NOAA-HATS	4	235	83	510	72	
Average ~40 samples	4.7	227.4	82.5	469.1	73.9	20.6
% accuracy	18%	-3%	-1%	-8%	3%	
% RSD	27%	9%	13%	11%	23%	18%

What can we learn about the analysis using Freons as sample monitoring compounds?

- Sensitivity of the system is stable
- Calibration standards are made correctly (not necessarily fractionation issues with low vapor pressure compounds)
- Sample was collected from outside air and sampled properly
  - Be careful of starting and stopping pressure in canisters to ensure proper delivery of sample (room air also has same Freon concentration)
- If system is behaving linearly, improve calibrations for instrument

Summary

- **Trace Concentrations in air analysis costs money, time**
- **Manage Data Quality Objectives to as high an RL as possible for project**
- **Control interferences and contamination.**
- **Carefully select calibration model for specific analytes depending on system conditions**
- **Monitor blanks in canisters and system**
- **Use banned CFC concentrations and other compounds in ambient samples to understand how system works and get idea of quality of sample**

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