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

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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/hrsadditio

Indoor V
Intrusi
Calculat

		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

*There are no
uncertainties lis
these target val
personal comm
with risk assess
orders of magni

ound	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
ein	107-02-8	n/a	n/a	0.009
alene; 45850	91-20-3	5.6	56	0.57
ylene dichloride	78-87-5	11	114	0.87
utadiene	106-99-0	15	151	0.90
onitrile	107-13-1	6.8	68	0.92
ene dibromide	106-93-4	0.22	2.2	1.2
yl bromide	74-83-9	n/a	n/a	1.3
ene	71-43-2	39	393	9.2
n tetrachloride	56-23-5	26	265	16
oform	67-66-3	n/a	n/a	20
es	1330-20-7	n/a	n/a	23
chloride	75-01-4	44	437	38
ichlorobenzene	106-46-7	15	152	133
ne	110-54-3	n/a	n/a	198
benzene	100-41-4	92	922	230
yl chloroform	71-55-6	n/a	n/a	926
ne	108-88-3	n/a	n/a	1326
2-tetrachloroethane	79-34-5	2.5	25	n/a
ene dichloride	107-06-2	9.5	95	n/a
chloroethylene	127-18-4	25	250	n/a
oroethylene	79-01-6	93	931	n/a
ylene chloride	75-09-2	608	6079	n/a

Ambient Air Health Comparison Values

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

Achieving these limits with high 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
- canisters or alternative containers
- sample train (passive regulators, connections, transfer lines, pumps)

Accuracy of calibration procedures

Carry over in instrument

- Naphthalene and other compounds with high vapor pressures

oid SIM unless very confident from interferenc

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

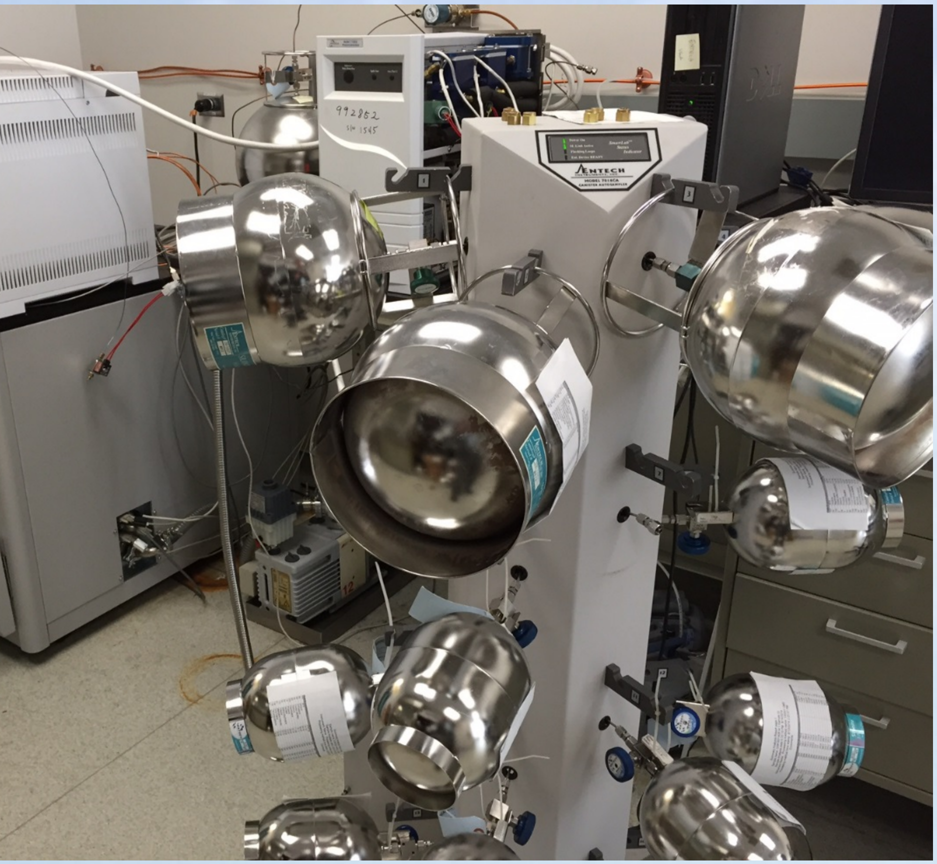
hat solutions are used to engineer out, minimize o al with contamination interferences?

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

Peggy

cold trap dehydration

Amelia



egasus HT, Agilent 7890,
7100, Entech 7016
ompounds 1 to 5 pg > 5 S/N FS

LECO TruTOF, Agilent 7890,
Entech 7200, Entech 7650
Most compounds 1 to 5 pg > 5

nister Cleaning

° C
cuum to 50 mtorr
sh to 20 psi whole air
2 minutes
peat 10- 20 times

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

anister Storage

anisters in zero air 20 psia
antitation report of blank cert.,
port with data file, and match to sample,
etected in blank and canister > 5 times blank

tion	MAX, pptv	n	Average, pptv
ne	232	13	36
	84	17	30
	83	6	34
lorobenzene	54	13	25
robenzene	37	15	4
nyl ketone	19	16	7
l	18	17	6
oride	17	1	
	16	10	13
e	15	15	0
	12	17	-1
e Chloride	12	17	5
robenzene	11	17	2
ne	9	6	4
	9	16	4
obutadiene	9	17	3
	9	17	2
ethylbenzene	8	11	2
robenzene	8	10	2
fluoromethane	7	11	2

Canister Blank D

3 day oven clea

Other compoun
under a max
concentration o
5 pptv.

17 cans some from so

cation	MAX pptv	average, pptv	count
nol	351	151	21
	295	242	21
	250	79	21
lene	109	-27	20
2-Dichloroethene	53	14	12
chlorobenzene	38	10	21
etate	30		15
	30	20	20
thyl ketone	29	17	21
oroethene	27	3	21
	23	13	21
difluoromethane	22	12	18
	21	4	21
loride	15	5	13
oroethane	14		4
orobenzene	12	4	21
one	12	10	8
ethene	11	4	17
3-Dichloropropene	10	7	12
orobutadiene	9	-1	21
orobenzene	9	2	21
omoethane	8	3	17
lrofuran	7		2
ichloropropene	7	5	9
orobenzene	7	1	19
	7	-6	21

Canister Blank Data

20 x cycle cleaning

Other compounds under a max concentration of 5 pptv.

21 cans

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.

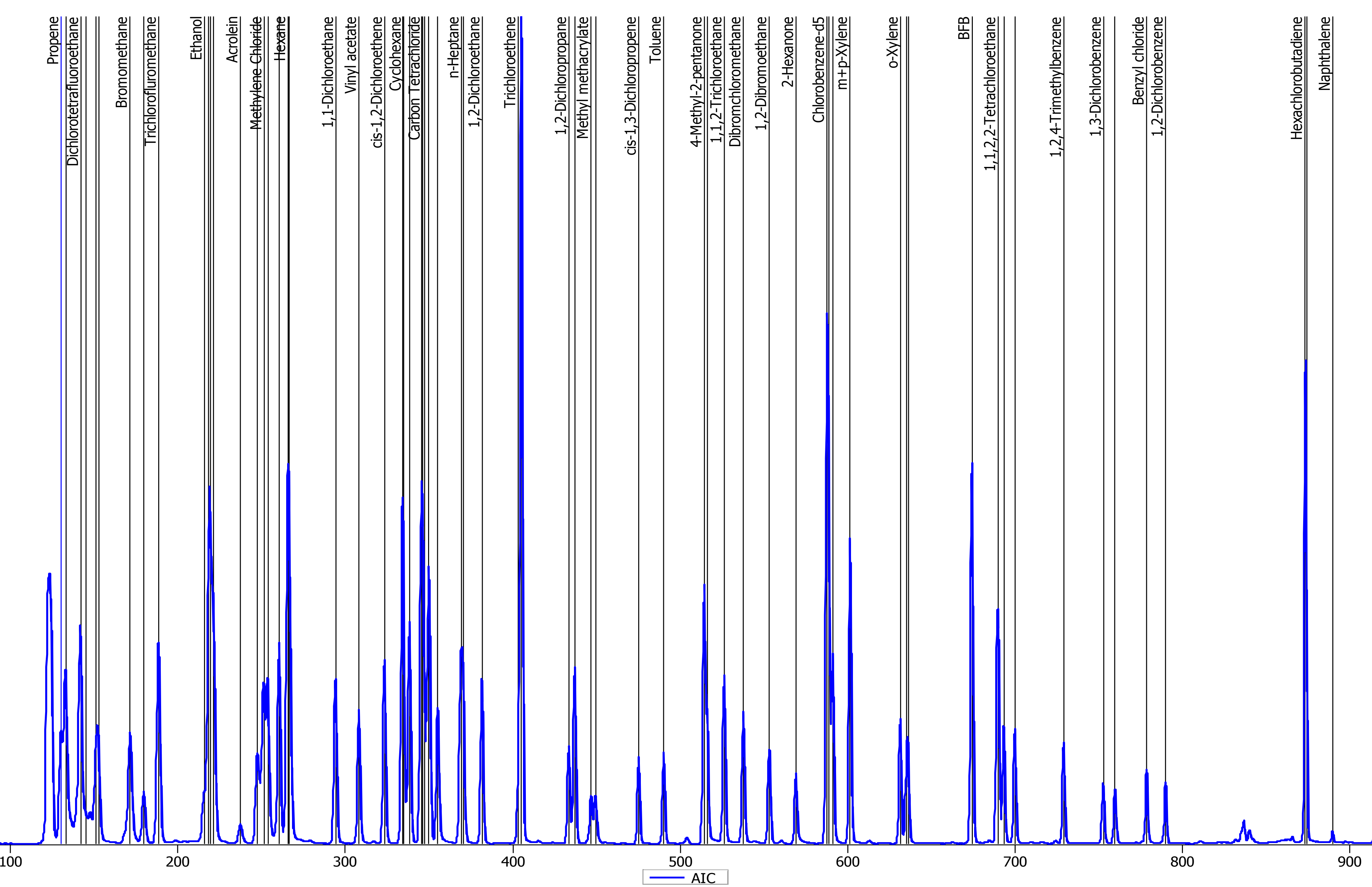
v to clean, and
 sampling
ns?
ality of sample is
/ as good as the
akest link in the
nple path

m Entech Instrument Catalogue

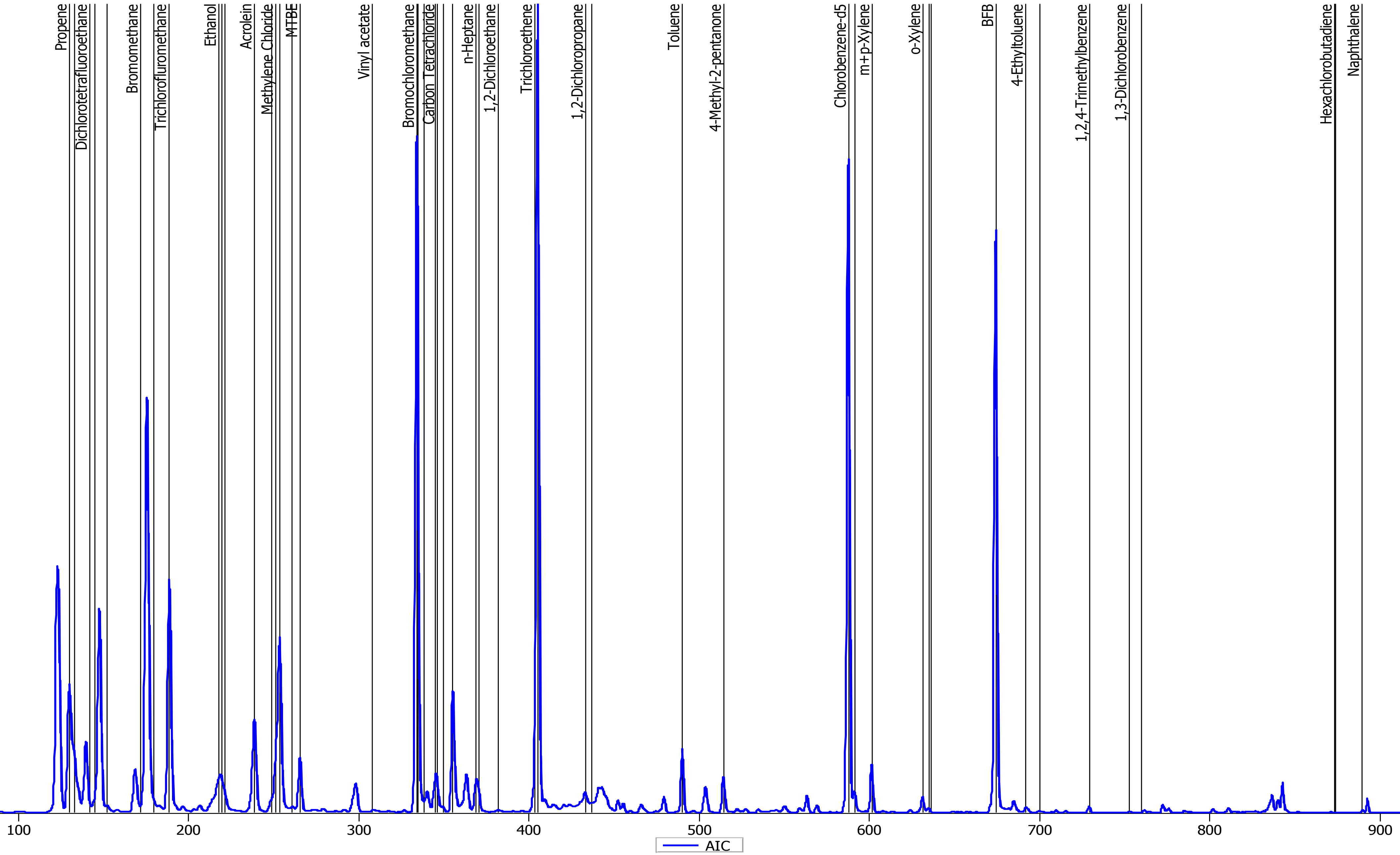
alibration Curve Fits

- se linear or quadratic
- orce through zero whenever possible
  - Makes it easy to see the interferences are present
  - Greatly improves accuracy at low concentrations
- eight calibration curve when not forcing through zero
- heck with % error between expected and calculated from calibration rve
  - ± 50 % error at RL, ± 30 % all points above,
  - Most levels should be tighter to about ± 10%

2 ppbv calibration standard   Rtx-VMS 30 m 0.25 mm ID, 1.4 µm



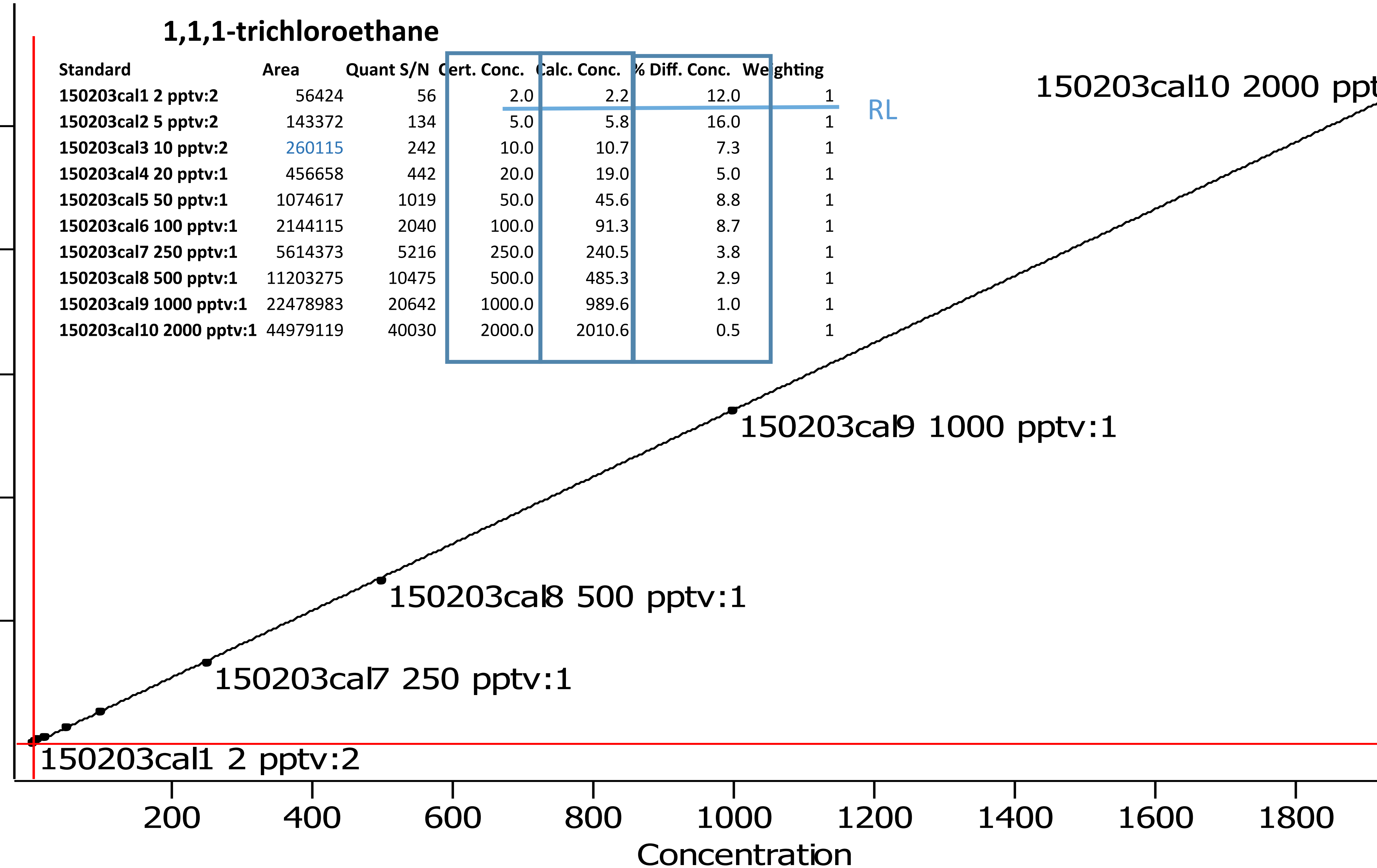
200 cc Integrated air sample



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



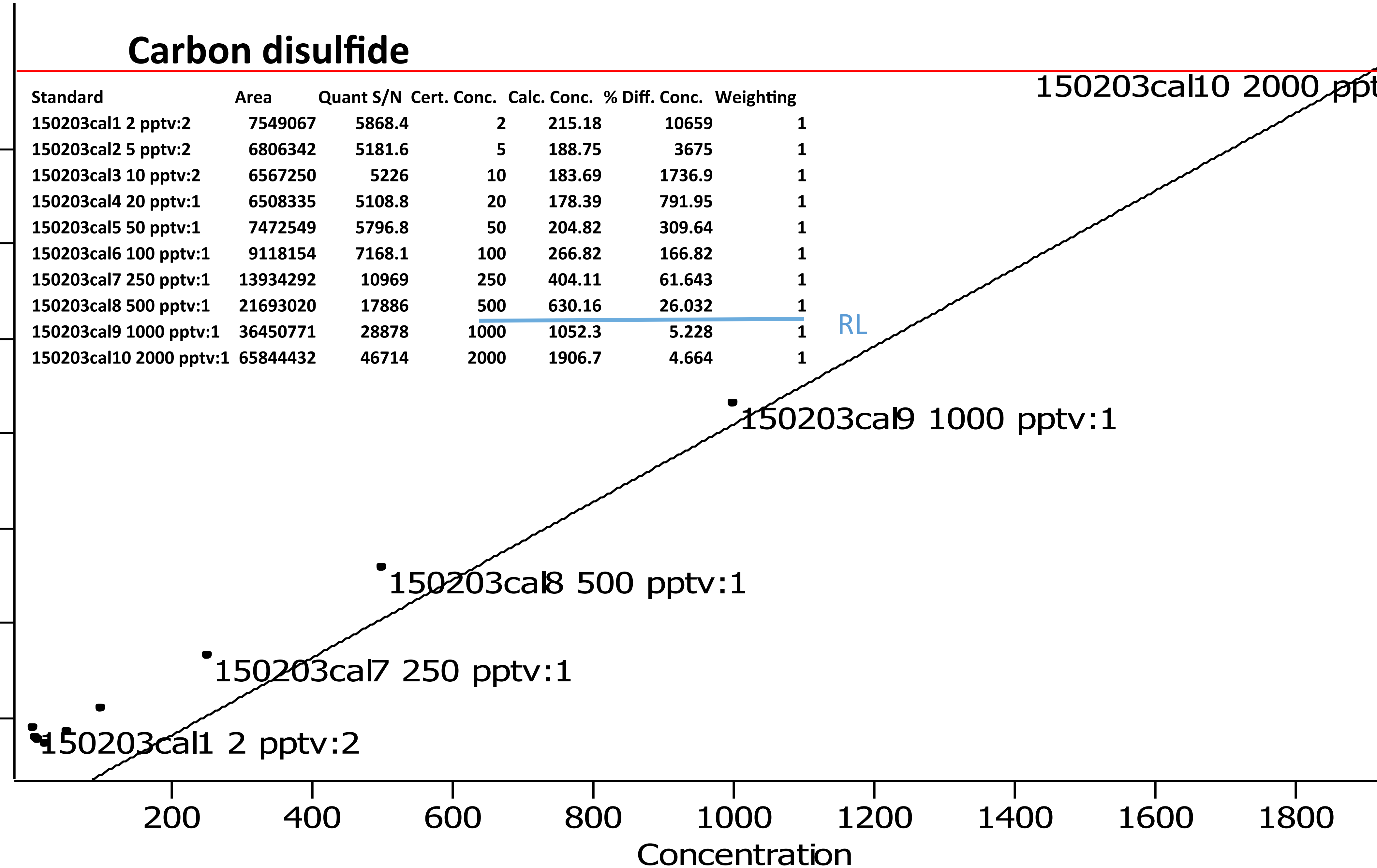
y= +0.00271438x + 0
r = 0.99994

Forced zero intercept

Carbon disulfide

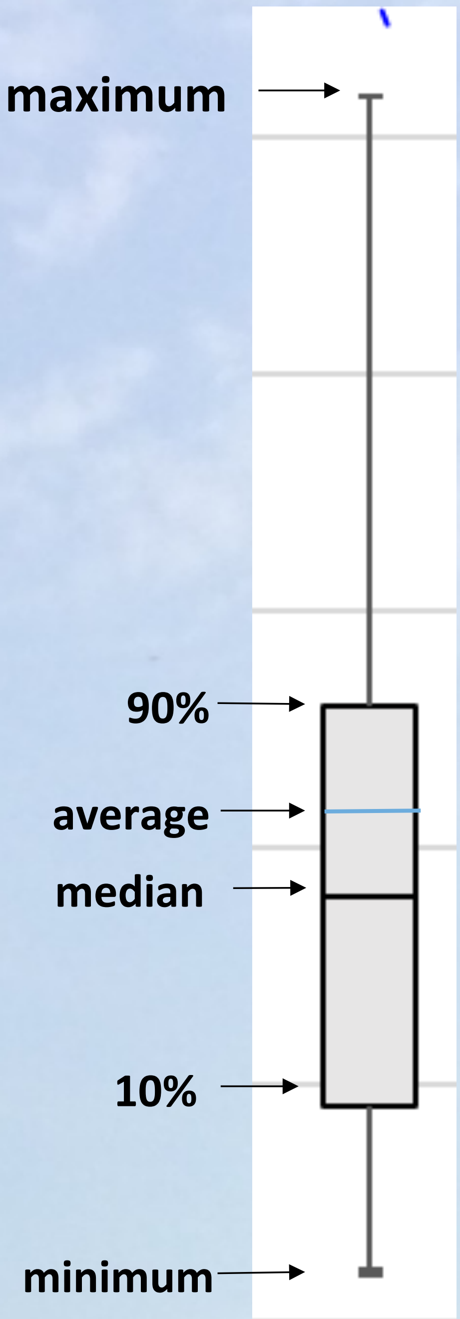
Standard	Area	Quant S/N	Cert. Conc.	Calc. Conc.	% Diff. Conc.	Weighting
150203cal1 2 pptv:2	7549067	5868.4	2	215.18	10659	1
150203cal2 5 pptv:2	6806342	5181.6	5	188.75	3675	1
150203cal3 10 pptv:2	6567250	5226	10	183.69	1736.9	1
150203cal4 20 pptv:1	6508335	5108.8	20	178.39	791.95	1
150203cal5 50 pptv:1	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



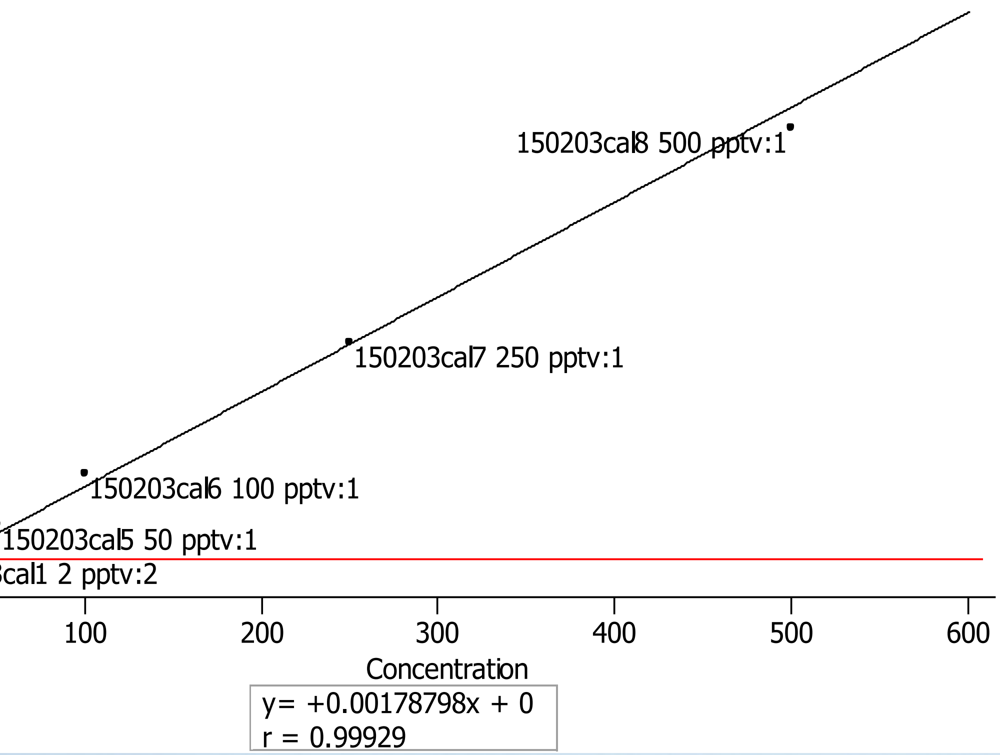
$y = +0.00821202x + 0$

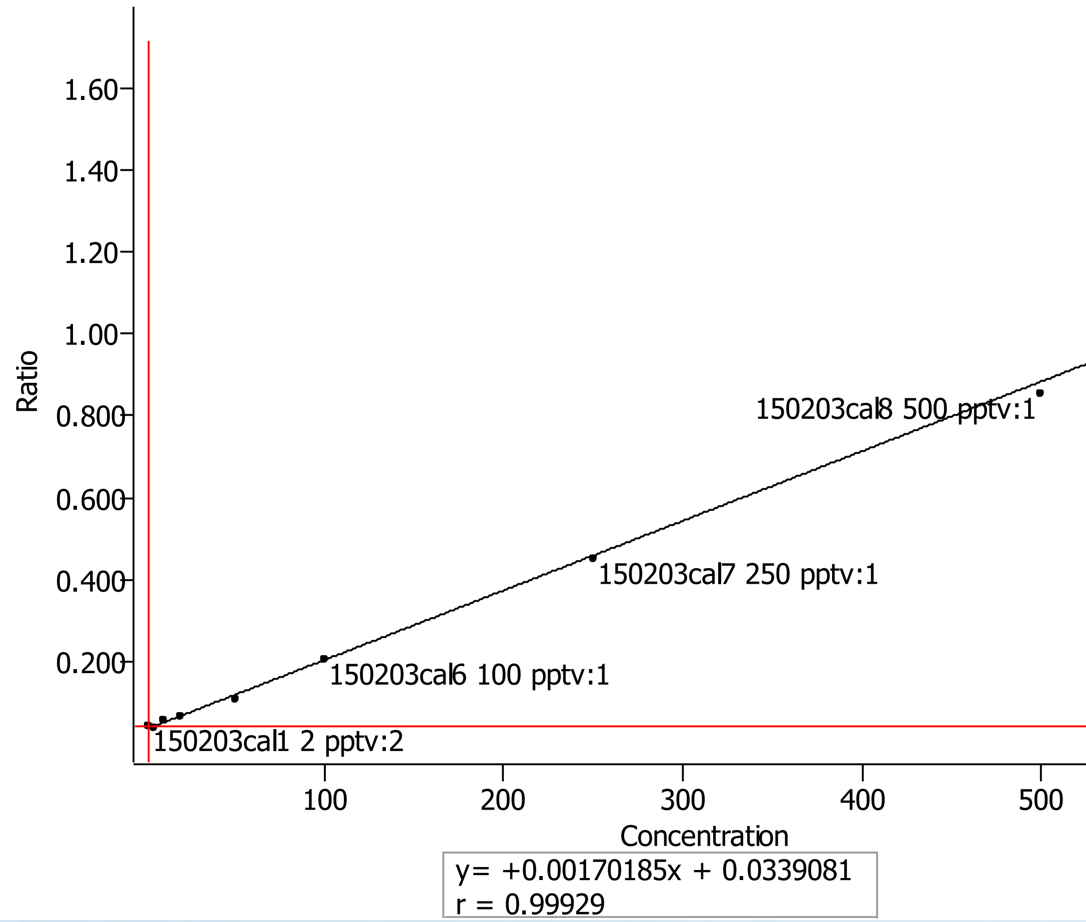
$r = 0.99960$

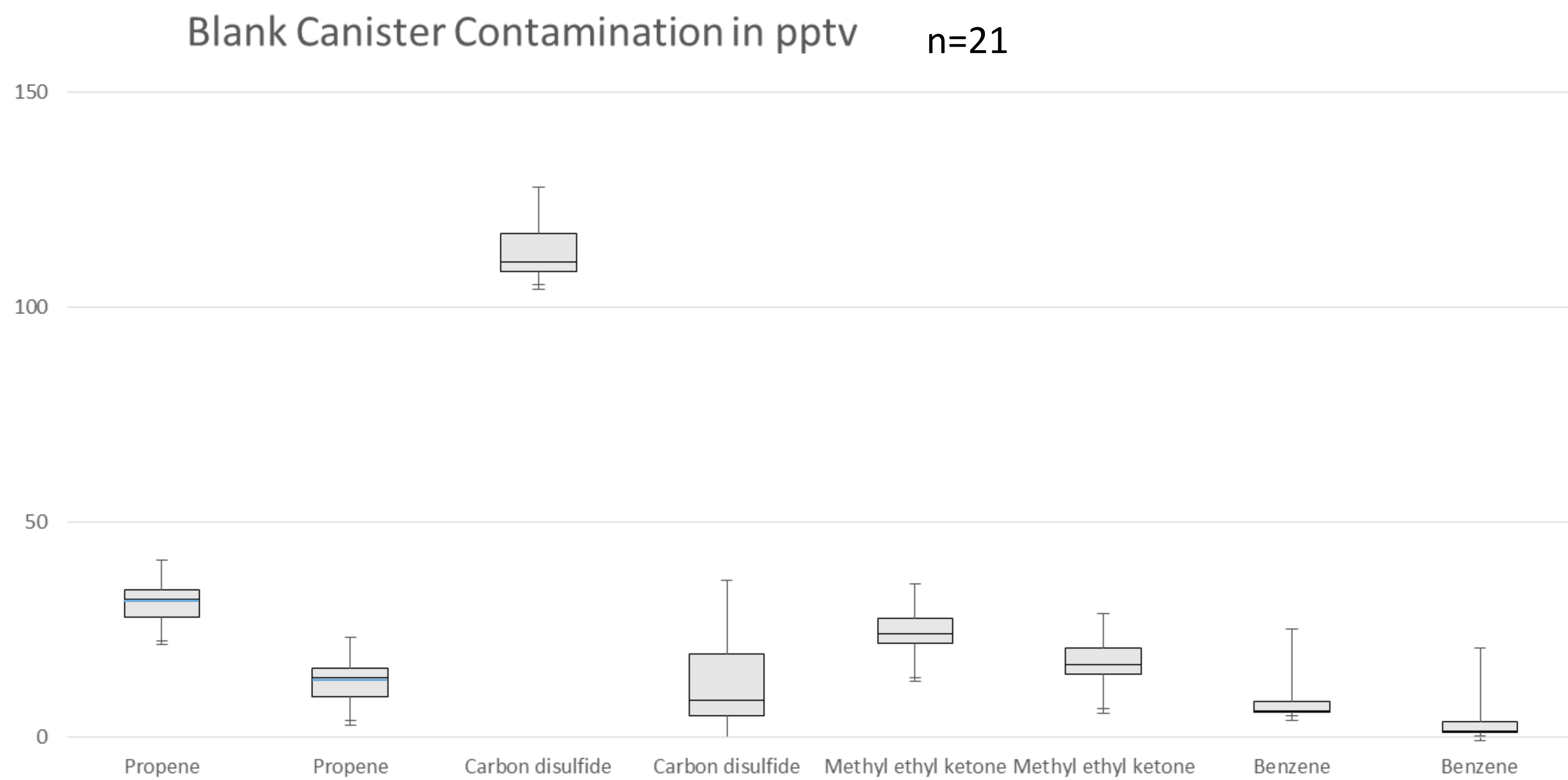


Box and Whisker Plot Legend
For blank canister data

opene Calibration Curves w and w/o forced ze







Propene calibration

Force Zero

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)

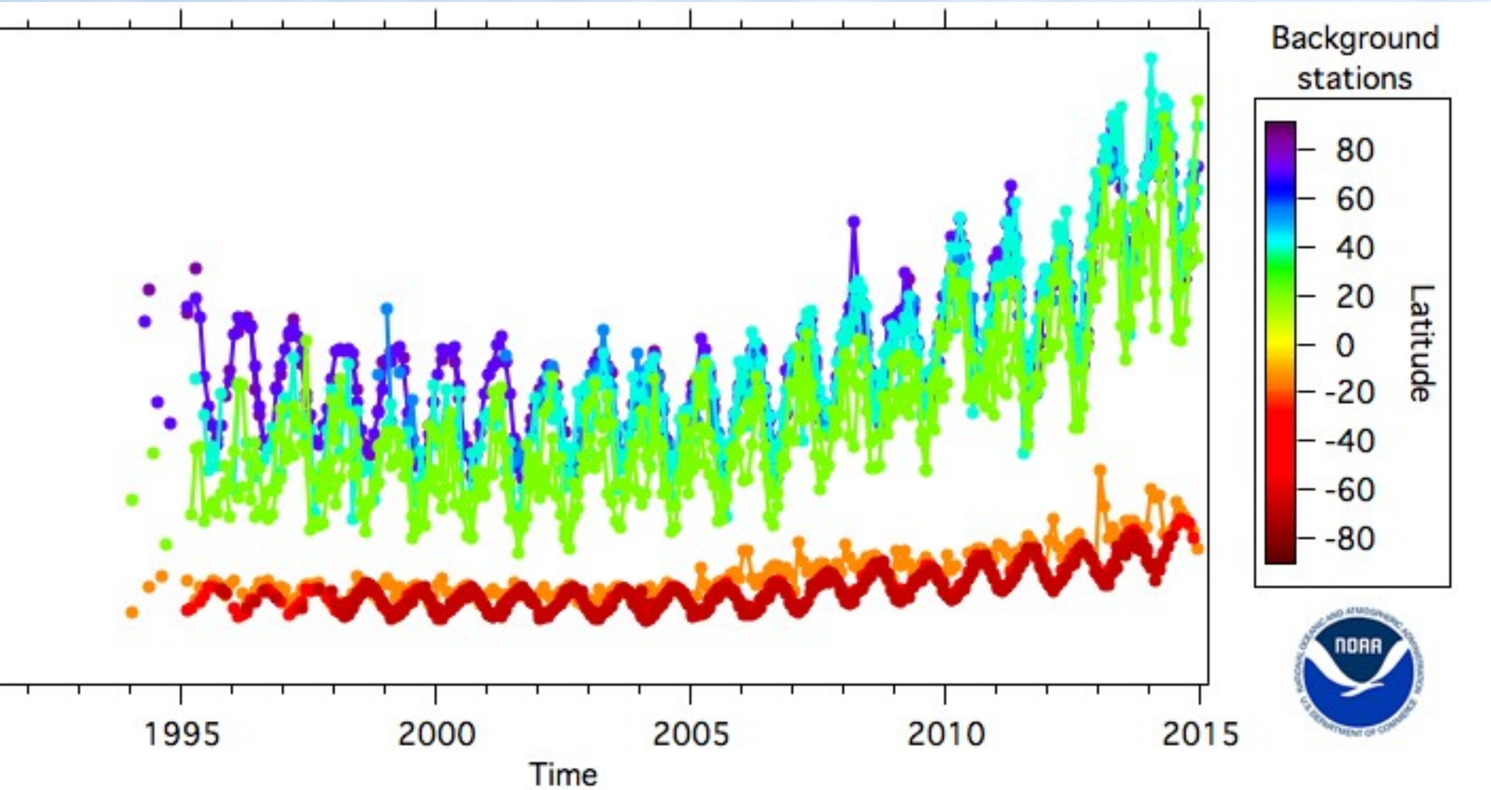
RL (Calculated Intercept: below 150203cal2 5 pptv:2)

Calculated Intercept

-50

-100

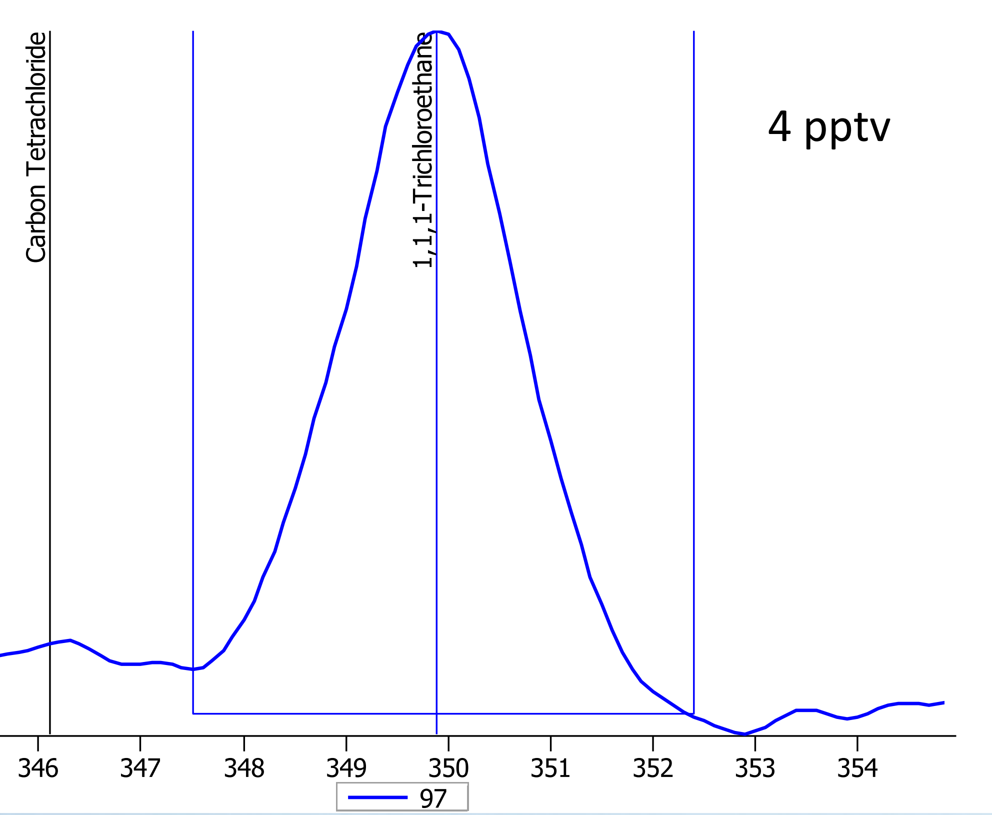
loromethane global temporal data and a sam with two calibration methods

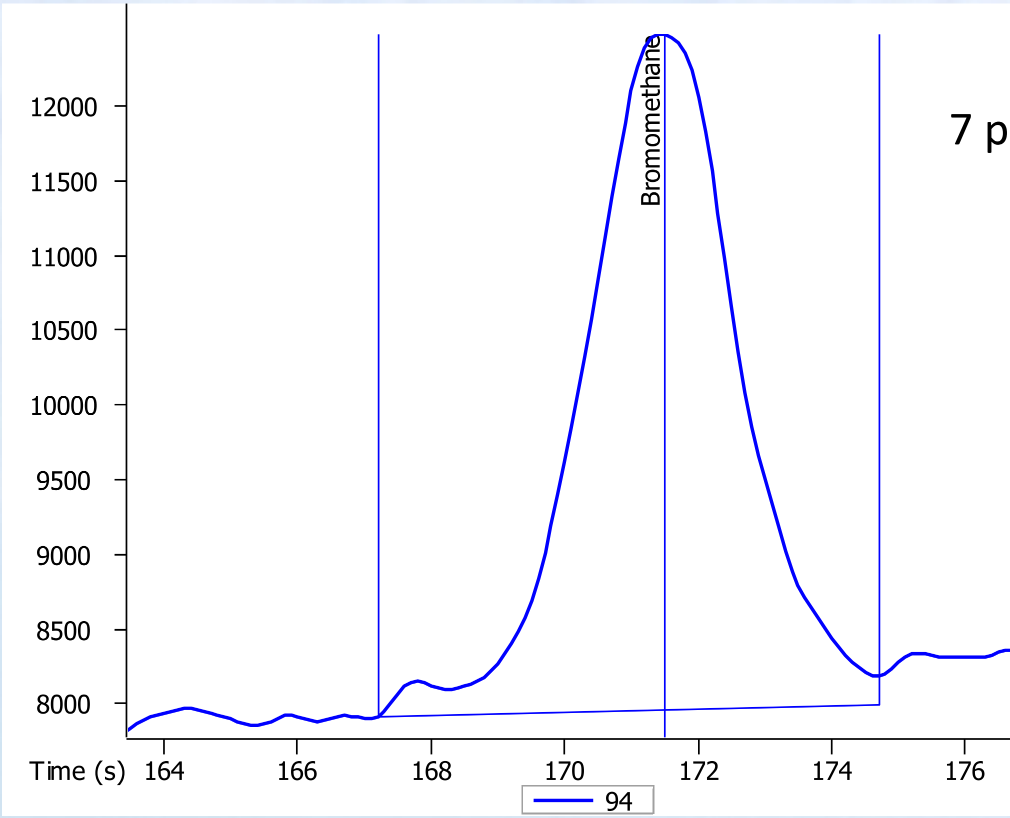


cal name	Sample Conce
141028 CFC lin 0 1W	
141028 CFC linear	
141028 CFC lin 0 1W	
141028 CFC linear	
141028 CFC lin 0 1W	
141028 CFC linear	
141028 CFC lin 0 1W	
141028 CFC linear	
141028 CFC lin 0 1W	
141028 CFC linear	
141028 CFC lin 0 1W	
141028 CFC linear	

Data from one week at site i
Calibration based RL 50 pptv
<blank> $_{0int}$ = 18 pptv, n=20
<blanks > $_{linear}$ = 0.6 pptv n=2

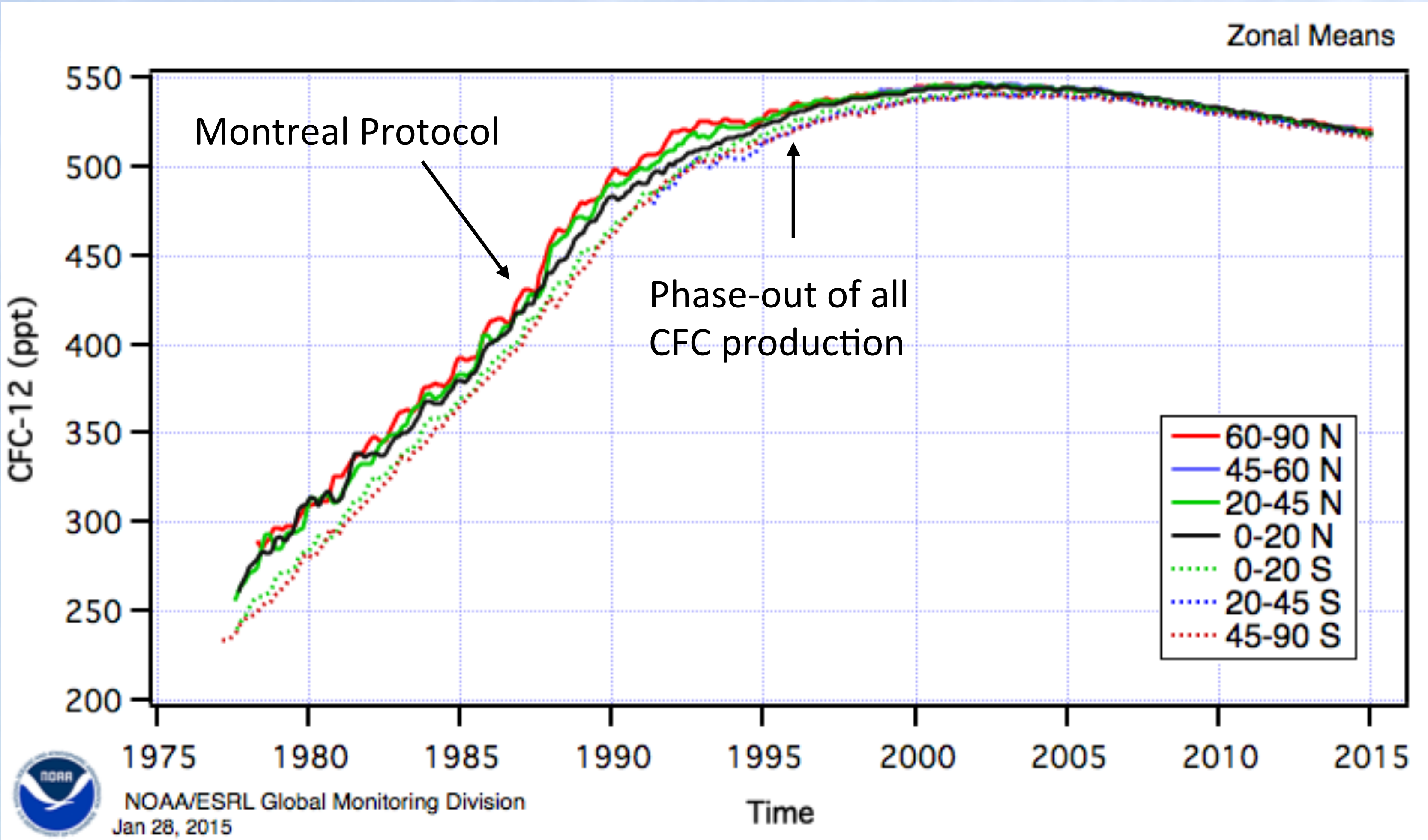
Two compounds that are in every ambient air sample at very low concentrations



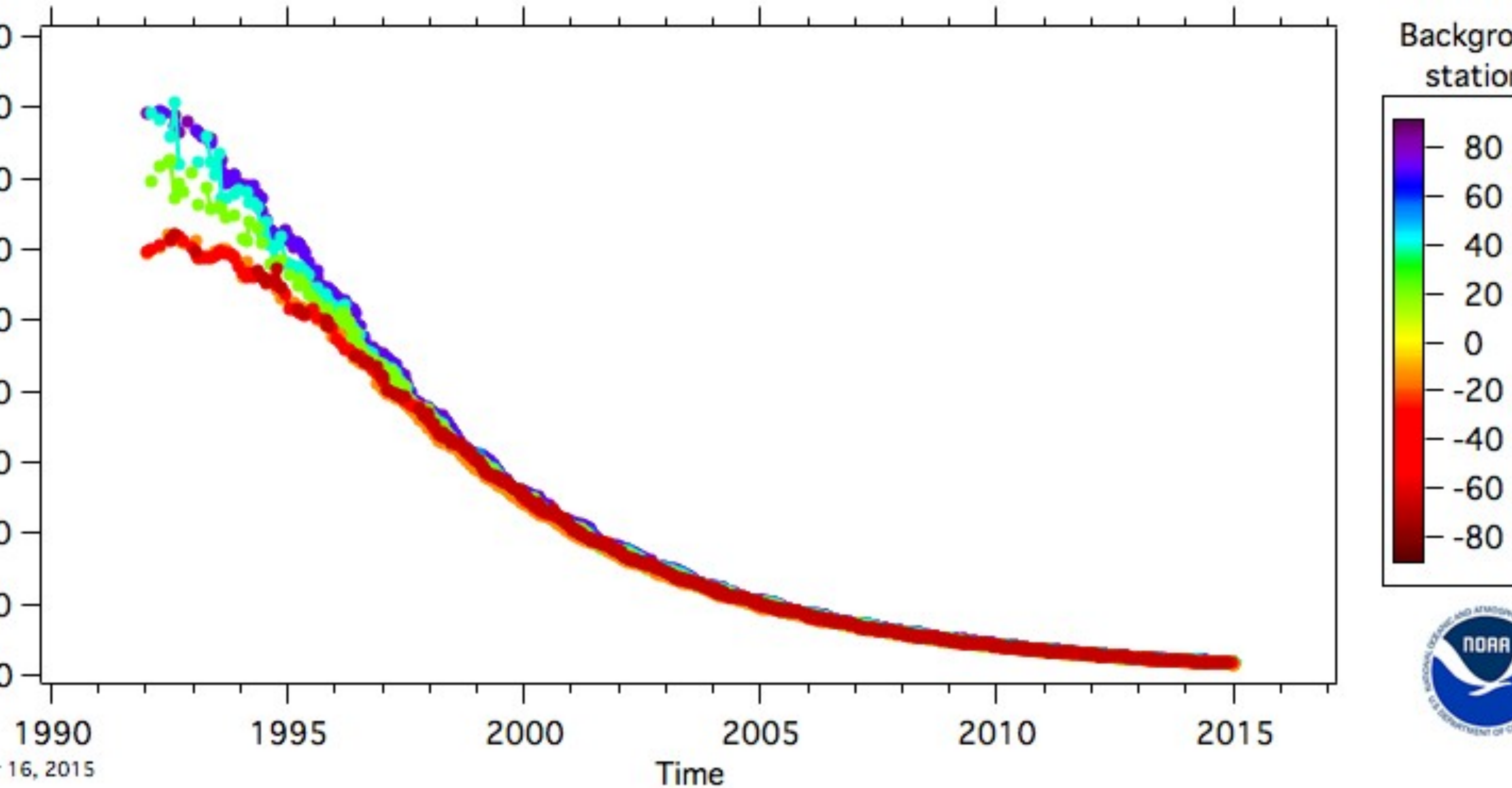


mL air sample

Freon 12 (dichlorodifluoromethane) vs. Year

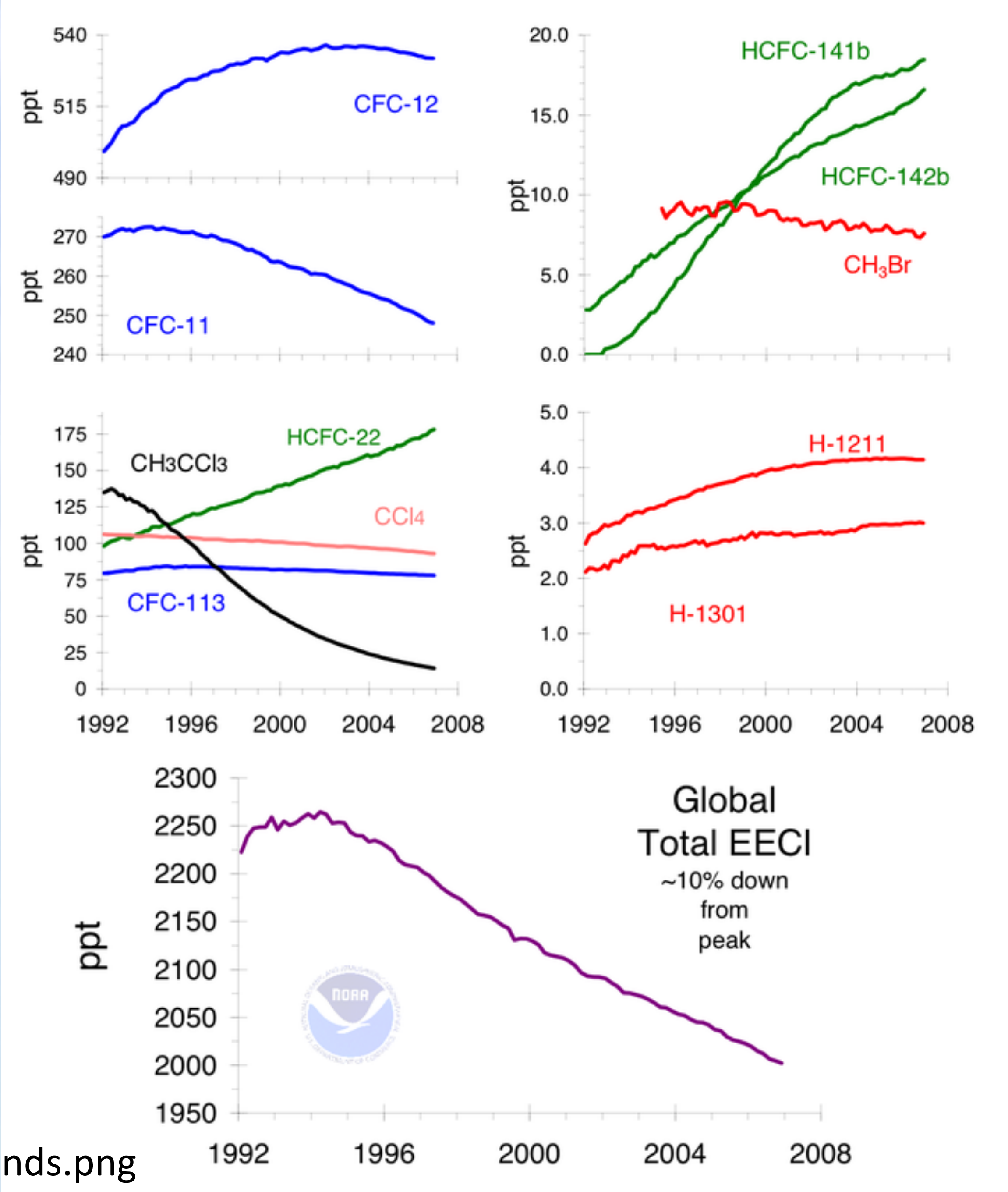


ww.esrl.noaa.gov/gmd/hats/combined/CFC12.html



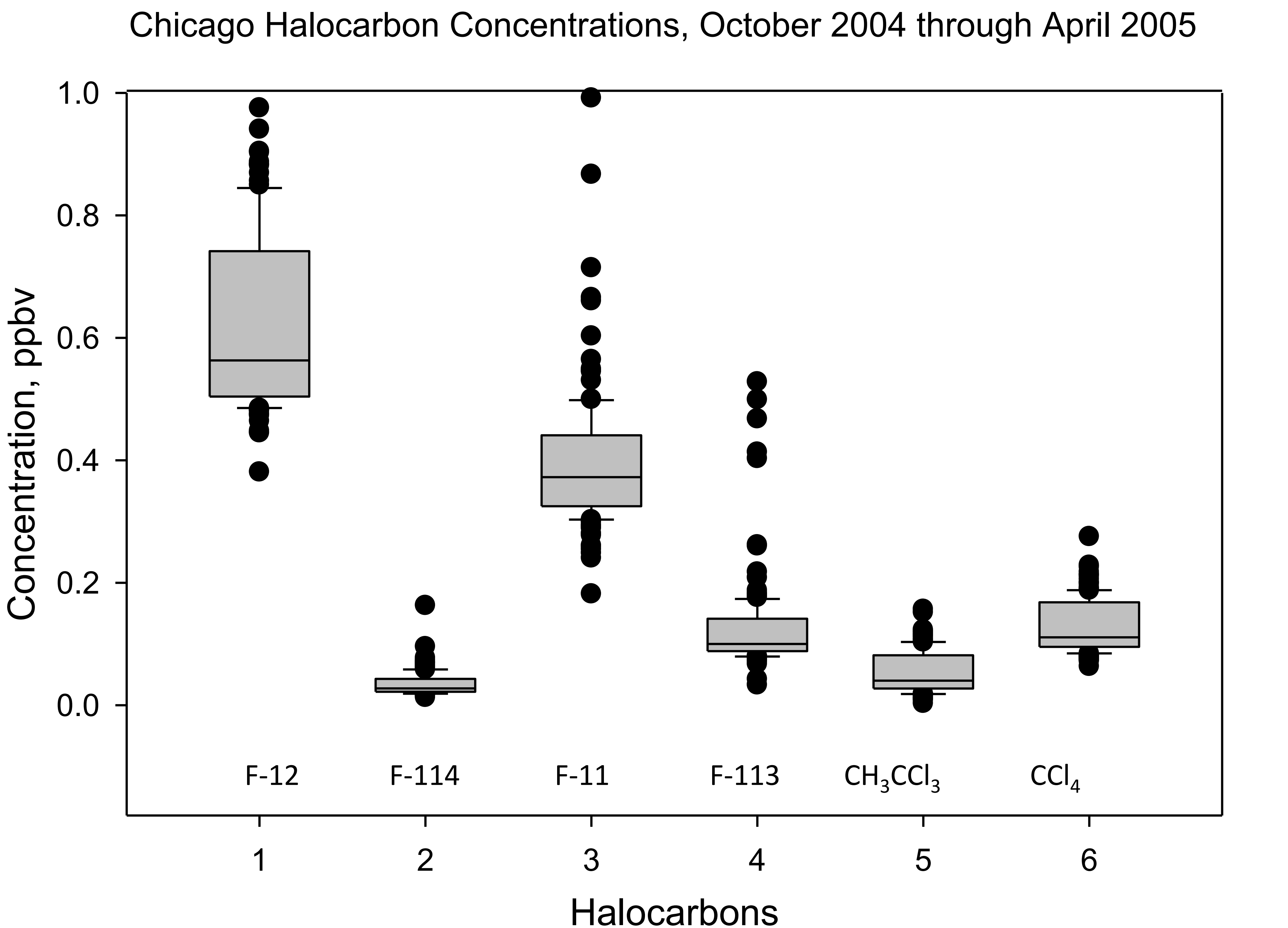
1990
1995
2000
2005
2010
2015
Time
16, 2015
Backgro
statio
80
60
40
20
0
-20
-40
-60
-80

locarbon
obal Trends

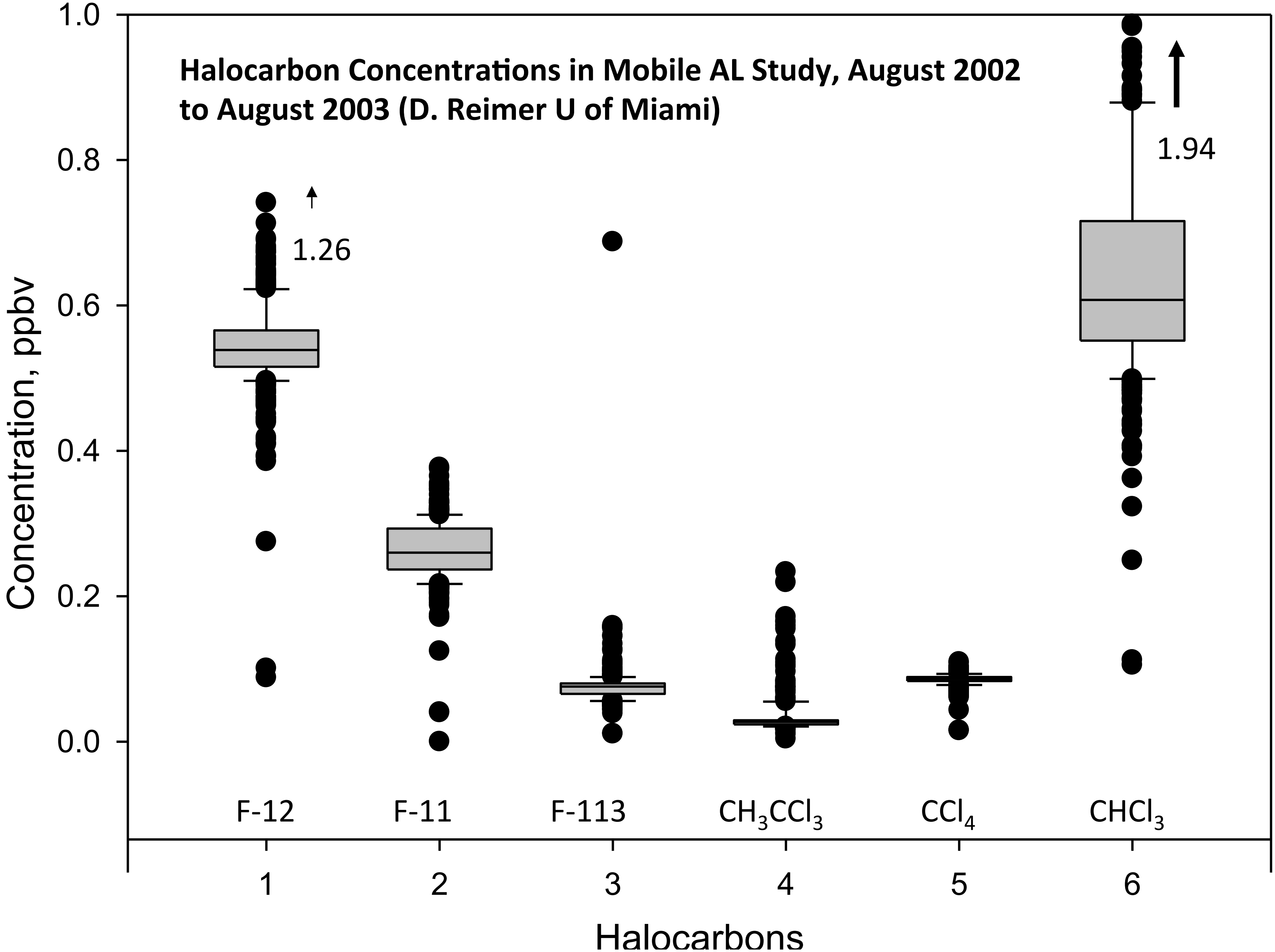


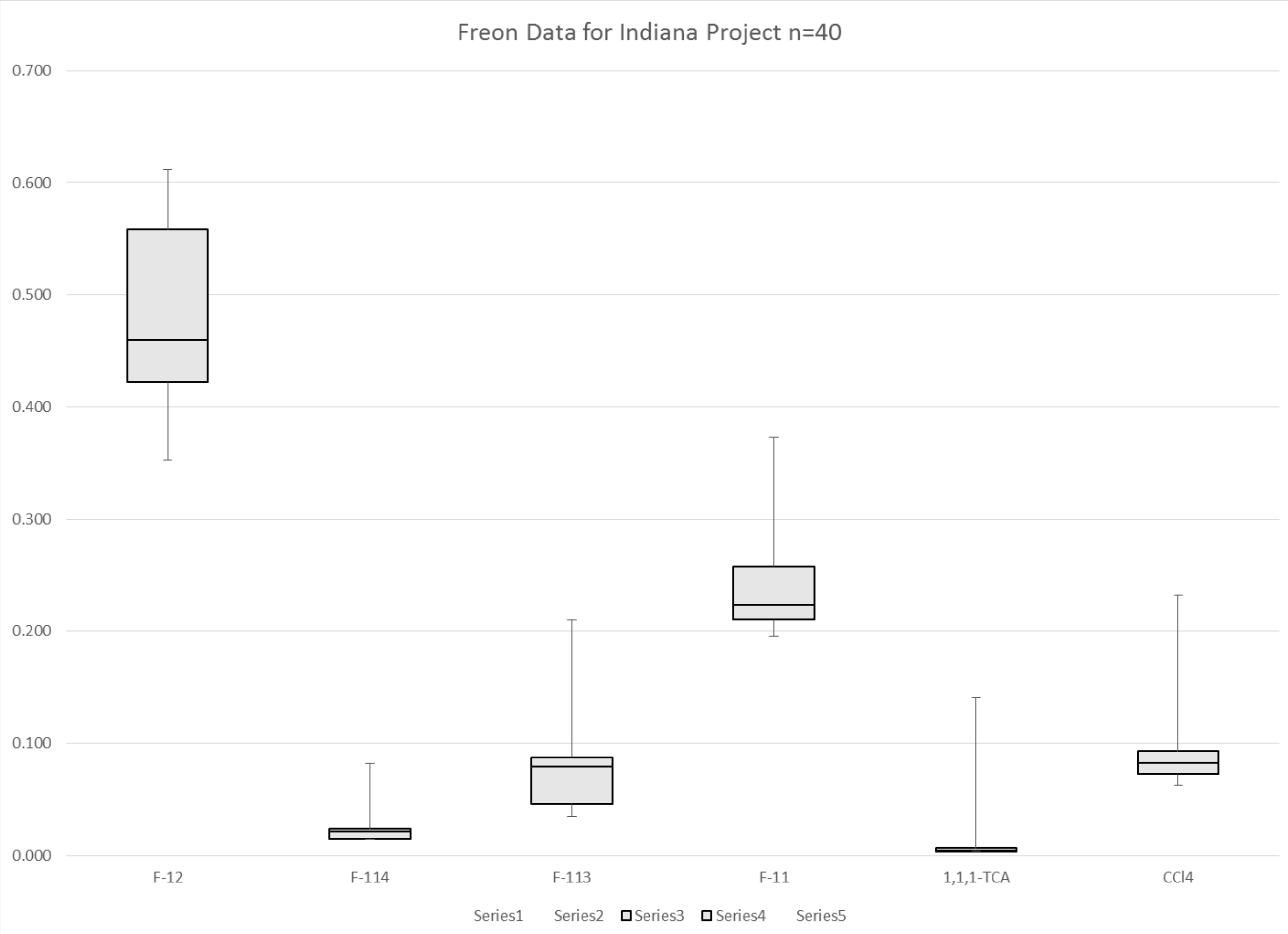
wikipedia.org/wiki/File:Ozone_cfc_trends.png

2002 Chicago Study for Freons as Surrogates



Chicago Halocarbon Concentrations, October 2004 through April 2005
Concentration, ppbv
1.0
0.8
0.6
0.4
0.2
0.0
F-12
F-114
F-11
F-113
CH_3CCl_3
CCl_4
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
1.0
0.8
0.6
0.4
0.2
0.0
1.26
1.94
F-12
F-11
F-113
CH_3CCl_3
CCl_4
$CHCl_3$
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%

Results of Freons with Various Curve Fits

	Quantification pptv	Sample	expected	% difference	pptv	Sample	expected
verage RF	1,1,1-Trichloroethane	3.33	4	17%	Carbon Tetrachloride	61.7	83
n 0 1W	1,1,1-Trichloroethane	4.05	4	-1%	Carbon Tetrachloride	71.1	83
n 0 invW	1,1,1-Trichloroethane	4.01	4	0%	Carbon Tetrachloride	70.2	83
near	1,1,1-Trichloroethane	-2.62	4	166%	Carbon Tetrachloride	62.6	83
near invW	1,1,1-Trichloroethane	-1.81	4	145%	Carbon Tetrachloride	64.6	83
verage RF	1,1,2-Trichloro-1,2,2-Trifluoroethane	61.3	72	15%	Dichlorodifluoromethane	348	510
n 0 1W	1,1,2-Trichloro-1,2,2-Trifluoroethane	74.6	72	-4%	Dichlorodifluoromethane	423	510
n 0 invW	1,1,2-Trichloro-1,2,2-Trifluoroethane	72.5	72	-1%	Dichlorodifluoromethane	407	510
near	1,1,2-Trichloro-1,2,2-Trifluoroethane	53.6	72	26%	Dichlorodifluoromethane	401	510
near invW	1,1,2-Trichloro-1,2,2-Trifluoroethane	61.6	72	14%	Dichlorodifluoromethane	405	510
verage RF	Dichlorotetrafluoroethane	19.7	20	2%	Trichlorofluromethane	171.0	235
n 0 1W	Dichlorotetrafluoroethane	19.7	20	2%	Trichlorofluromethane	192.4	235
n 0 invW	Dichlorotetrafluoroethane	19.8	20	1%	Trichlorofluromethane	190.6	235
near	Dichlorotetrafluoroethane	19.7	20	2%	Trichlorofluromethane	185.5	235
near invW	Dichlorotetrafluoroethane	19.8	20	1%	Trichlorofluromethane	187.2	235

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

ng calibration force through zero vs. non force through

Force through zero

- Gives better results with very low concentration and extremely little backgrour 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.

Vhat can we learn about the analysis using reons 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**

Appreciation

- US EPA R5 Laboratory personnel for support
- Dr. Daniel Riemer for data and information
- US EPA R5 Air and Radiation Division especially Dr. Motria Caudill