Vertical Profiles of Reactive Gaseous Mercury during TORERO
plus a few other things about Hg in the atmosphere

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Atmospheric Hg

- Two stable oxidation states
- Elemental: Hg^0 (>95%): GEM
  - unreactive, insoluble, low deposition rate
  - long atmospheric lifetime: 6 month – 1 year
  - global background [Hg^0] = 1 – 2 ng m^{-3}
  - Northern Hemisphere: 1.5 ng m^{-3}
  - Southern hemisphere: 1 ng m^{-3}
  - Atmospheric [Hg^0] has risen by a factor of 3 in the last 100 years

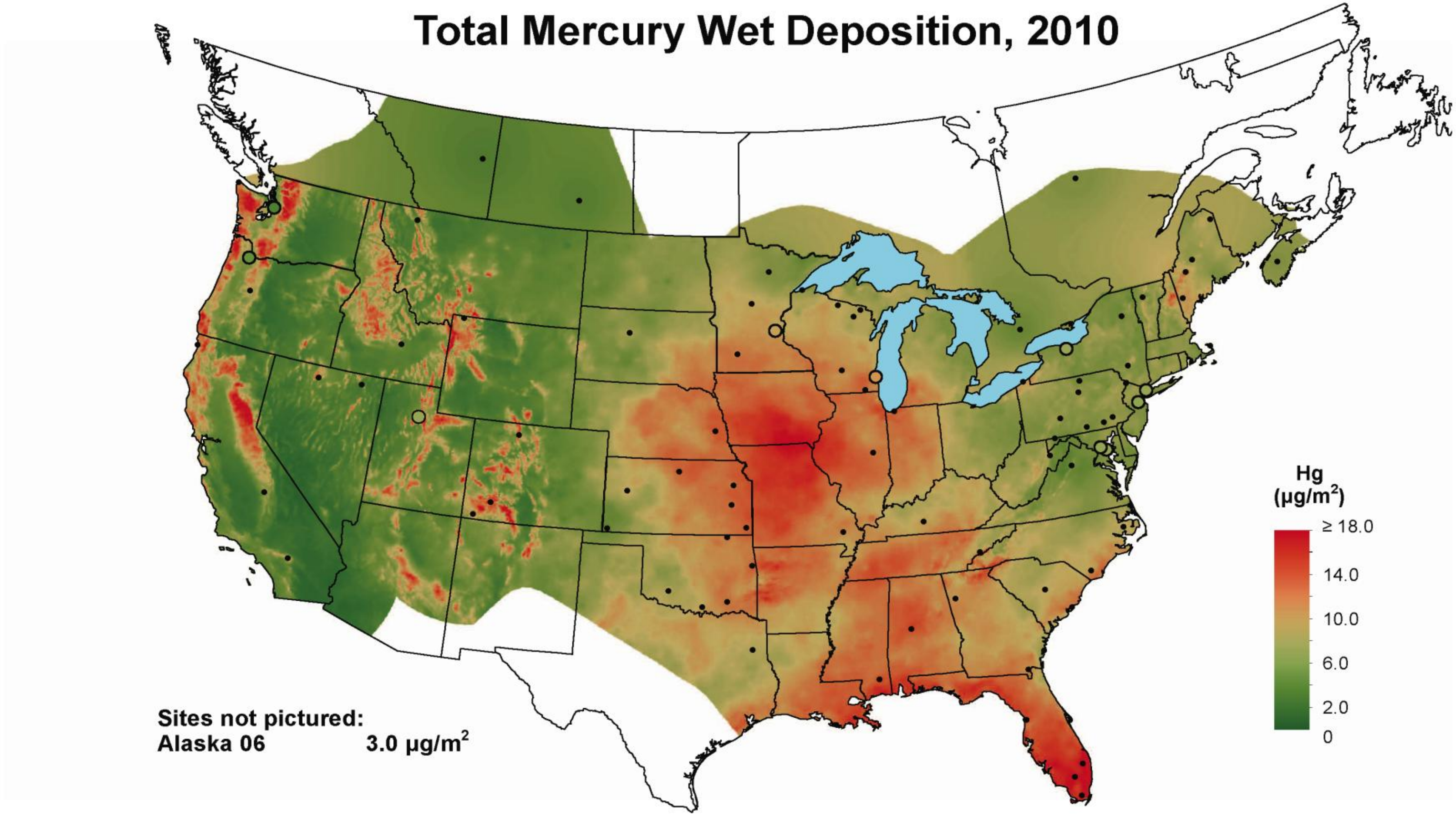
Reactive Gaseous Mercury (RGM)

- Operationally defined term: mercury species that collect on a KCl denuder
- Major species ?: $HgCl_2$, $HgBr_2$
- Water soluble
- Easily washed out of the atmosphere resulting in increased local deposition
- Concentrations are normally low (3 ± 11 pg m^{-3} in MBL : Sorensen et al. 2010)
- BUT higher values observed in subsiding air (Mt. Bachelor : Reno) and AMDE's

ATMOSPHERIC Hg CHEMISTRY

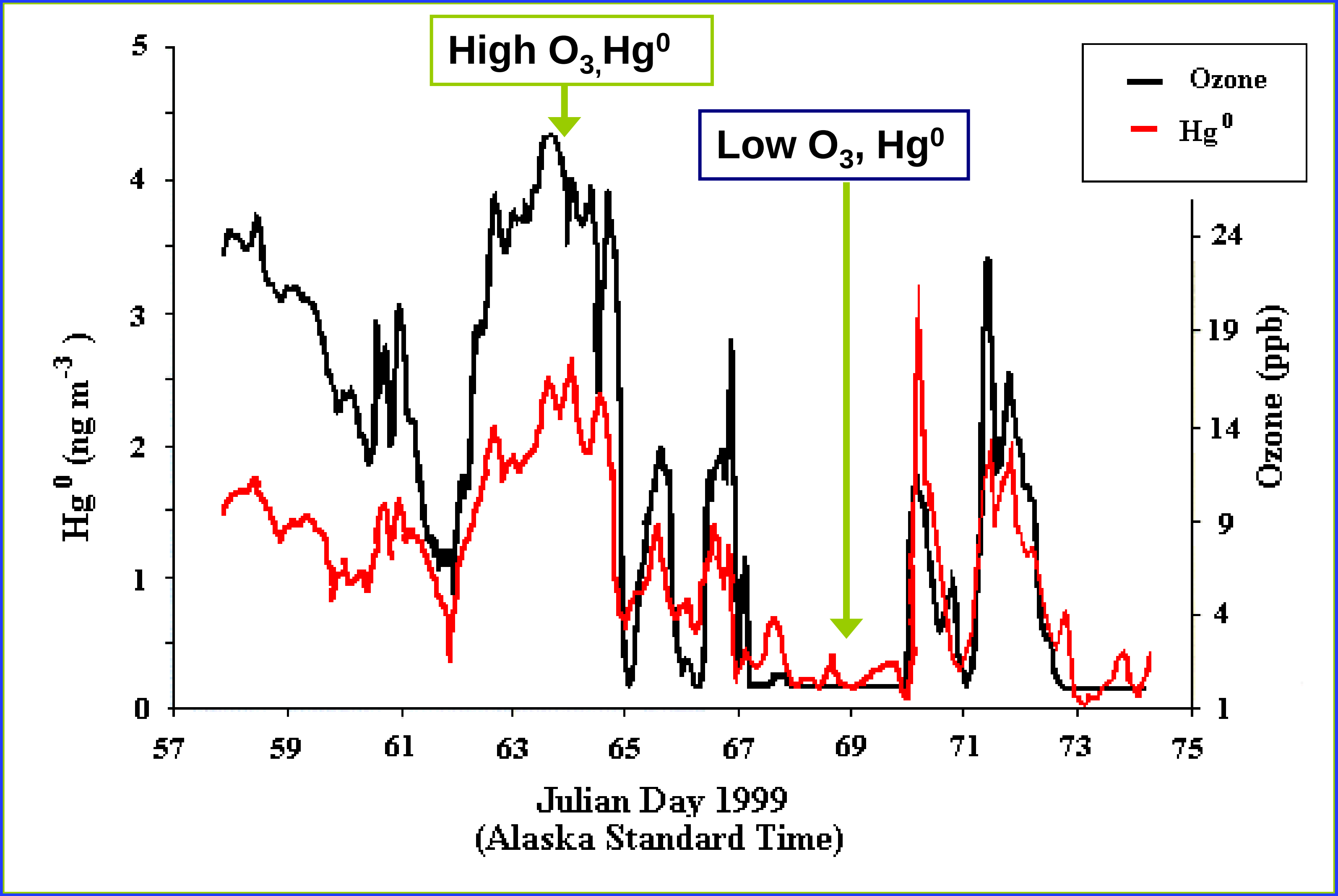
- Not well understood!!
- Deposition: Peculiar pattern of wet deposition with very high values in the SE USA
- Atmospheric Mercury Depletion Events (AMDE's). Sporadic examples of very fast oxidation chemistry at poles and elsewhere

Total Mercury Wet Deposition, 2010



National Atmospheric Deposition Program/Mercury Deposition Network
http://nadp.isws.illinois.edu

Barrow Arctic Mercury Study



Lindberg et al (2002)

Arctic Hg depletion

- No Hg depletion before sunrise

Strong correlation between O_3 and Hg depletion

Reactive gaseous mercury (RGM) is rising
during depletion of Hg(0)

Depletion event is triggered by sunrise

Halogen (Br) chemistry is likely candidate

Non-Arctic Chemistry

Peleg et al. [3] diurnal cycles of mercury, ozone, and BrO near the Dead Sea, Israel.

Mona Loa, Mount Bachelor, Reno evidence for elevated RGM in the free and upper troposphere.

MBL observations of diurnal variation in production of RGM

What is the mechanism of Atmospheric Hg^0 Oxidation?

- HOx (OH; O_3) vs Halogen initiated oxidation
- Global oxidation of background pool vs local anthropogenic emissions?

Halogen recombination

$Hg(0) + X + M \Rightarrow HgX + M$

$X = Br, Cl$

Three body recombination,

P dependent

Measurable rate coefficient

HgX stable molecule, monitor spectroscopically, study chemistry

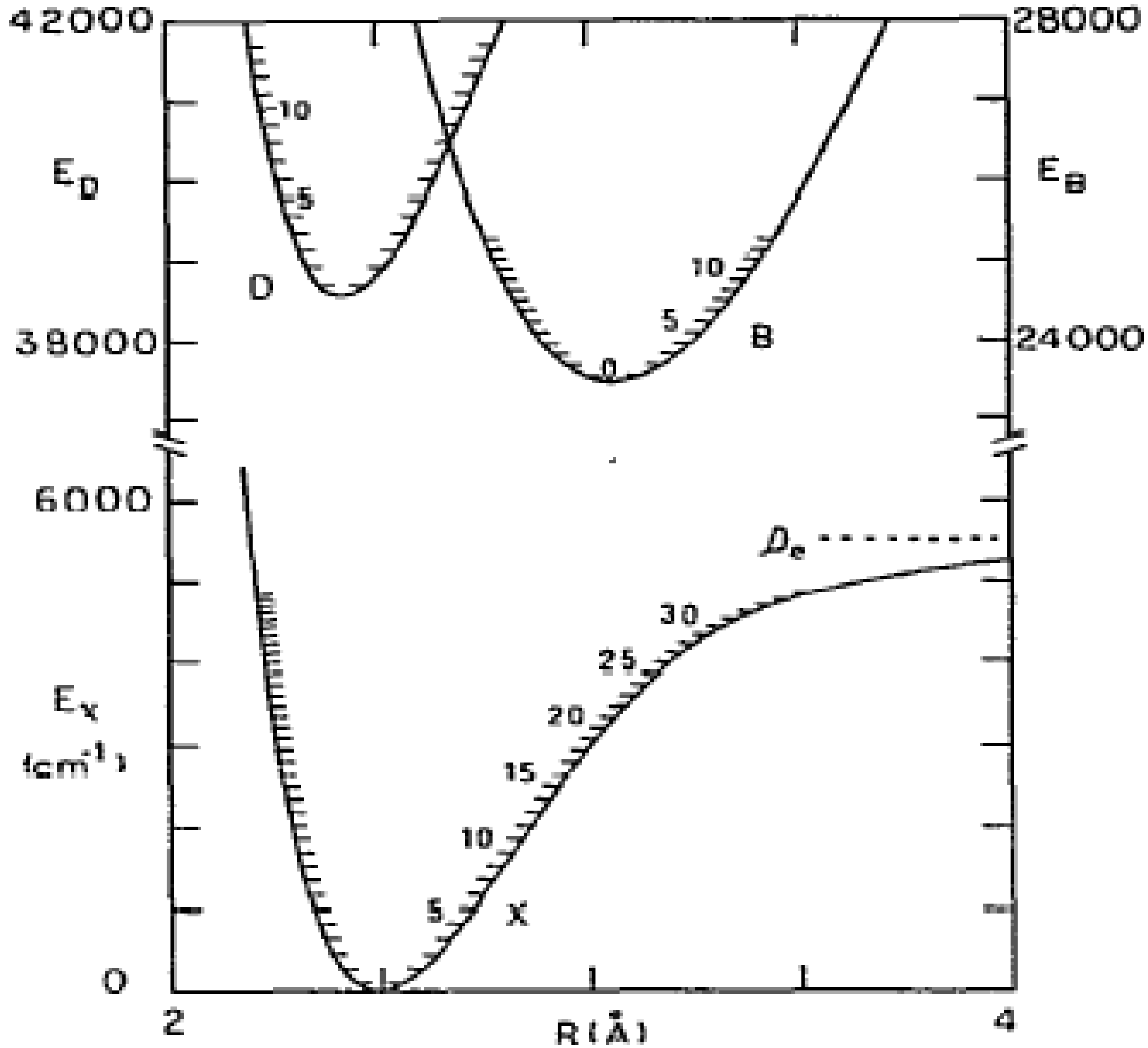
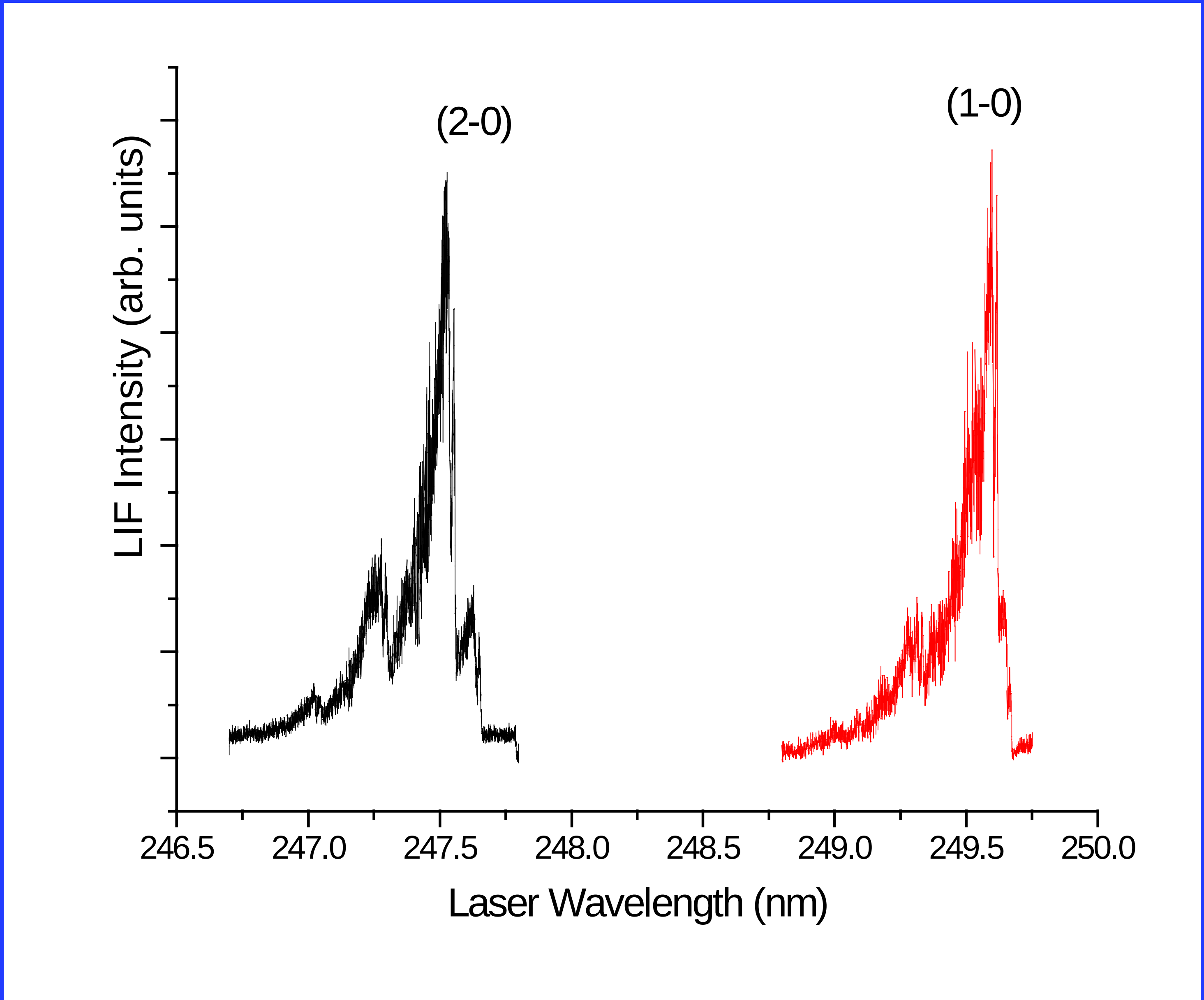
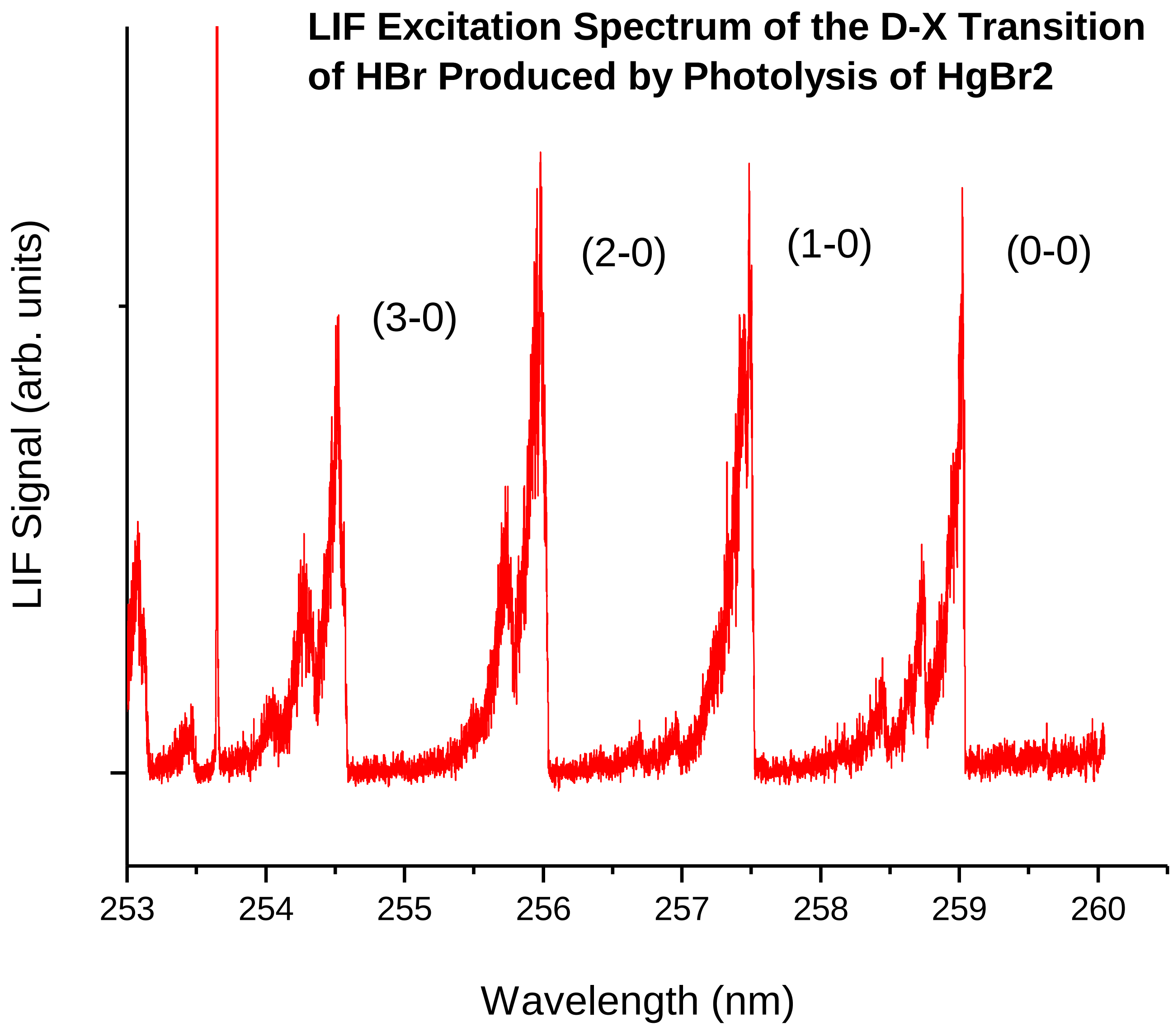


Fig. 1. Potential diagram for HgBr, showing levels of the X, B, and D states spanned by the present analysis. Note the different energy scales for all three states.

LIF Spectra of the $D^2\Pi$- $X^2\Sigma$ (2-0) and (1-0) Bands of HgCl after Photolysis of $HgCl_2$





LIF Excitation Spectrum of the D-X Transition
of HBr Produced by Photolysis of HgBr2
LIF Signal (arb. units)
(3-0)
(2-0)
(1-0)
(0-0)
253
254
255
256
257
258
259
260
Wavelength (nm)

$Hg(0) + Br + M \Rightarrow HgBr + M$

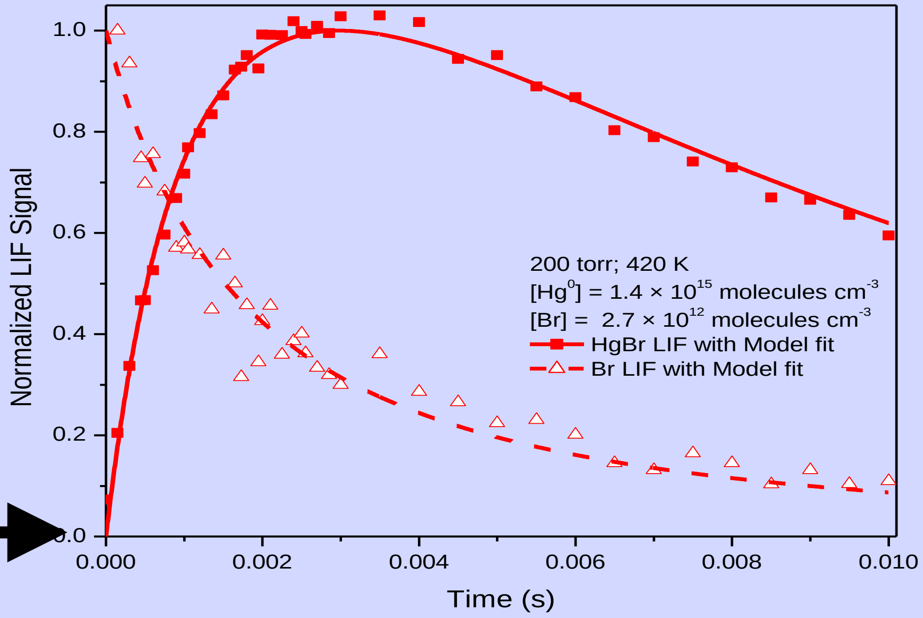
Important in AMDE's?

Global Oxidant for Hg(0)?

Perhaps the best defined Hg(0) rate coeficient, uncertainty less than a factor of 10 !

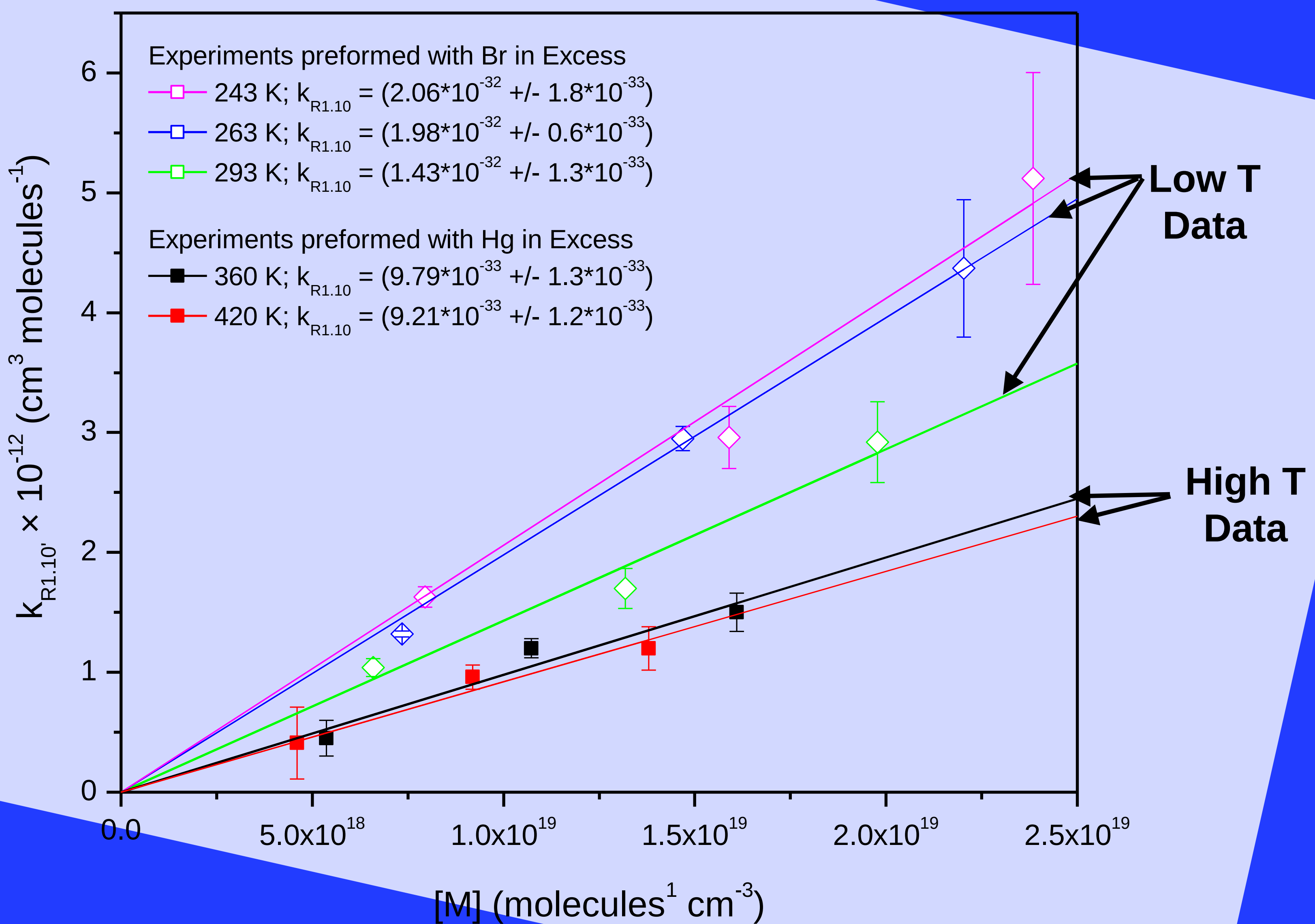
Numerical Integration

$$\frac{d[Br]}{dt} = -k_1[Br][CF_3] - k_2[Br] - k_3[Br][Hg] - k_5[HgBr][Br] + k_4[HgBr]$$



$$\frac{d[HgBr]}{dt} = k_3[Br][Hg] - k_5[HgBr][Br] - k_4[HgBr]$$

Hg + Br + M→ HgBr + M

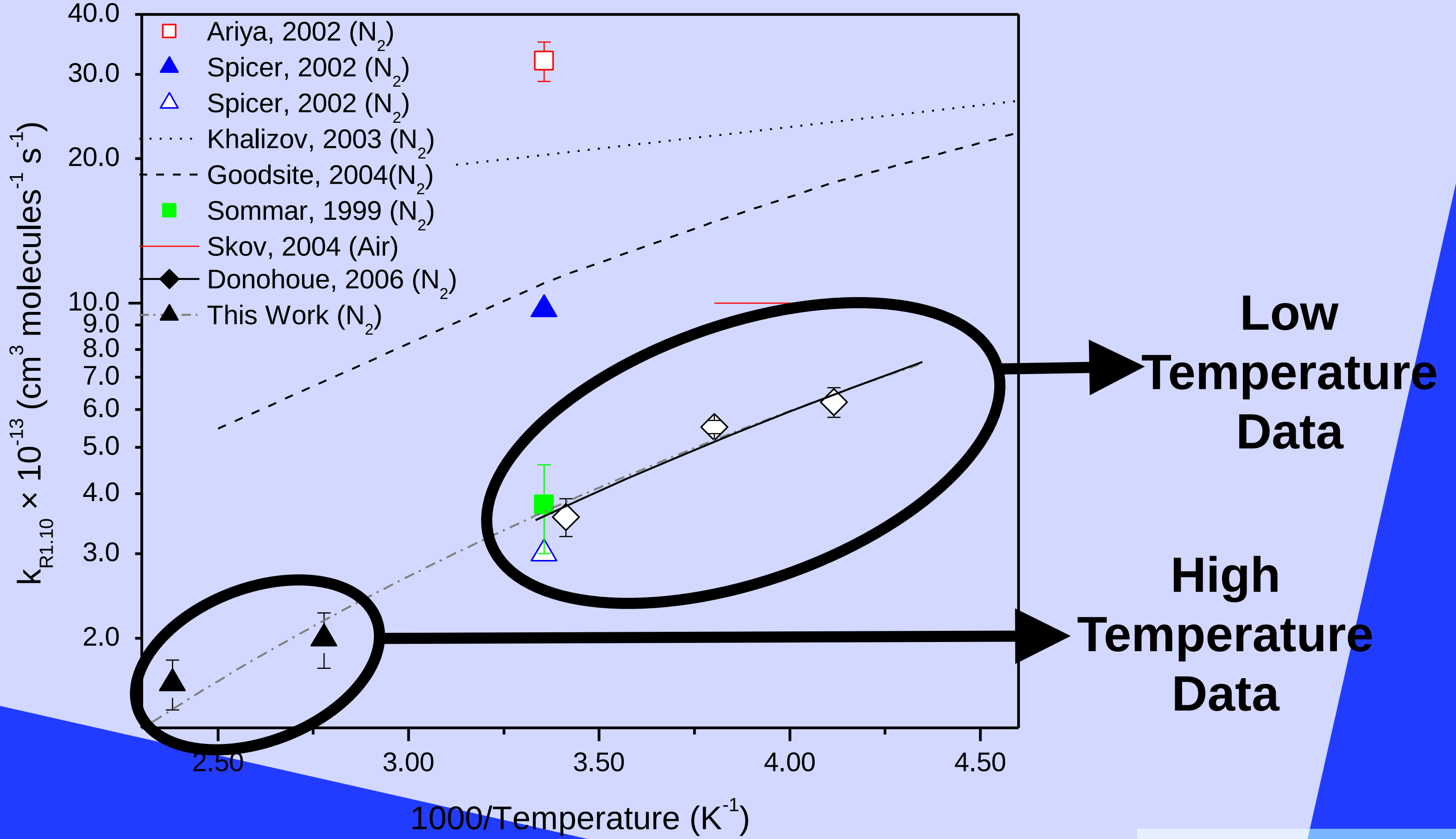


Experiments preformed with Br in Excess
243 K; k_R1.10 = (2.06*10^-32 +/- 1.8*10^-33)
263 K; k_R1.10 = (1.98*10^-32 +/- 0.6*10^-33)
293 K; k_R1.10 = (1.43*10^-32 +/- 1.3*10^-33)
Experiments preformed with Hg in Excess
360 K; k_R1.10 = (9.79*10^-33 +/- 1.3*10^-33)
420 K; k_R1.10 = (9.21*10^-33 +/- 1.2*10^-33)
Low T Data
High T Data
k_R1.10' × 10^-12 (cm^3 molecules^-1)
[M] (molecules^1 cm^-3)
0.0
5.0x10^18
1.0x10^19
1.5x10^19
2.0x10^19
2.5x10^19
0
1
2
3
4
5
6

Hg + Br + M→ HgBr + M

3rd Order Plot

$$k_{3,N_2}(243-420K) = (1.49 \pm 0.34) \times 10^{-32} \times \left(\frac{T}{298}\right)^{-(1.76\pm0.5)}$$



$Hg + Br \rightarrow HgBr$ (1)

$HgBr \rightarrow Hg + Br$ (2)

$HgBr + Br \rightarrow BrHgBr$ (3)

τ due to reaction with Br =

$$t_{Hg} = \frac{\frac{k_2}{k_3} + [Br]}{k_1 [Br]^2}$$

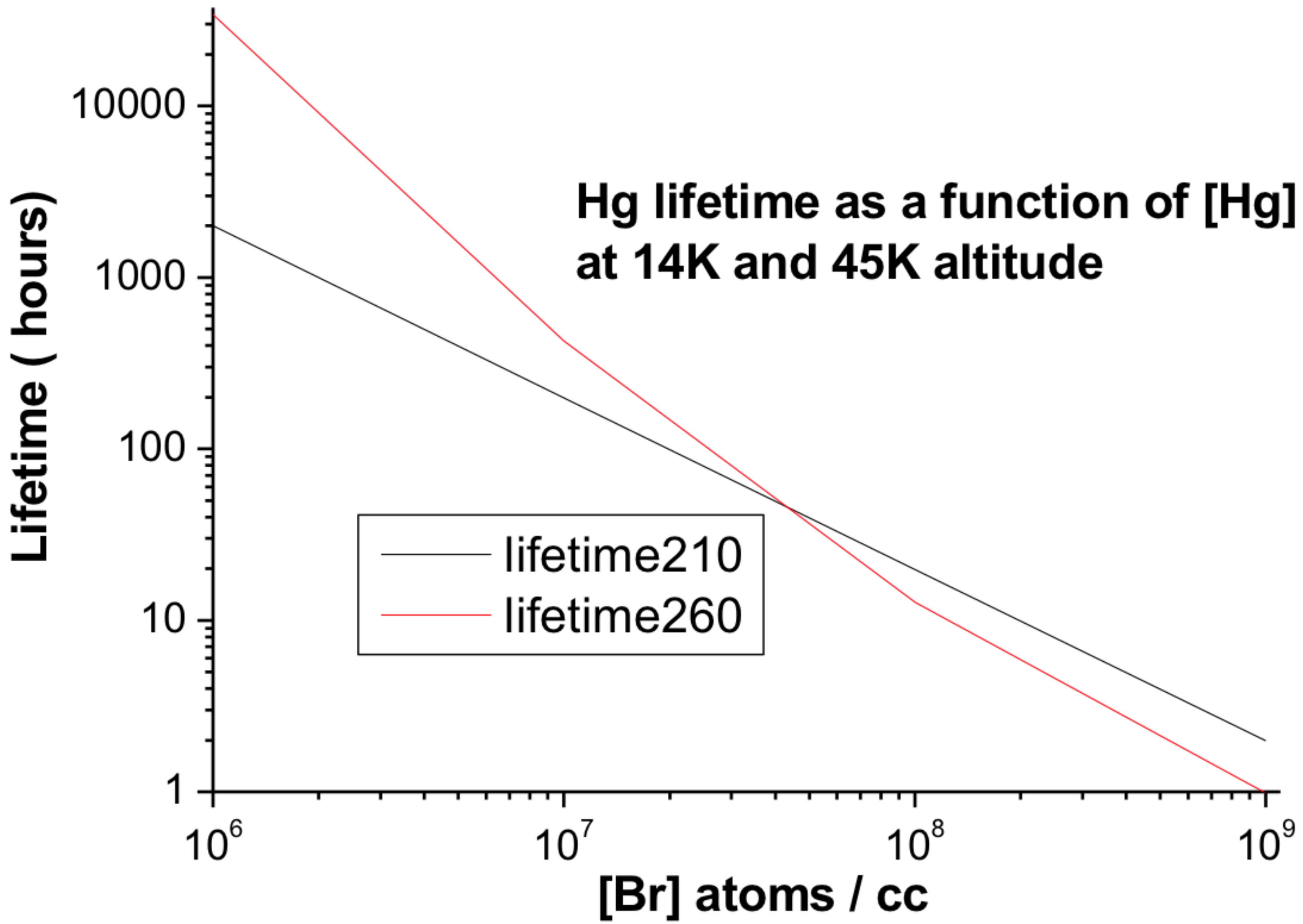
At 210K, 110 Torr

τ due to reaction with Br =

$$t_{Hg} = \frac{1}{k_1 [Br]}$$

At [Br] = 1e9 : 2 hours

1e8 : 20 hours



Hg lifetime as a function of [Hg]
at 14K and 45K altitude
Lifetime (hours)
10000
1000
100
10
1
lifetime210
lifetime260
10^6
10^7
10^8
10^9
[Br] atoms / cc

Hg on TOREO

- Late, “bootlegged” addition to project
- Challenges from fiscal and personnel issues

- Thanks to Rainer, RAF staff for getting us onboard

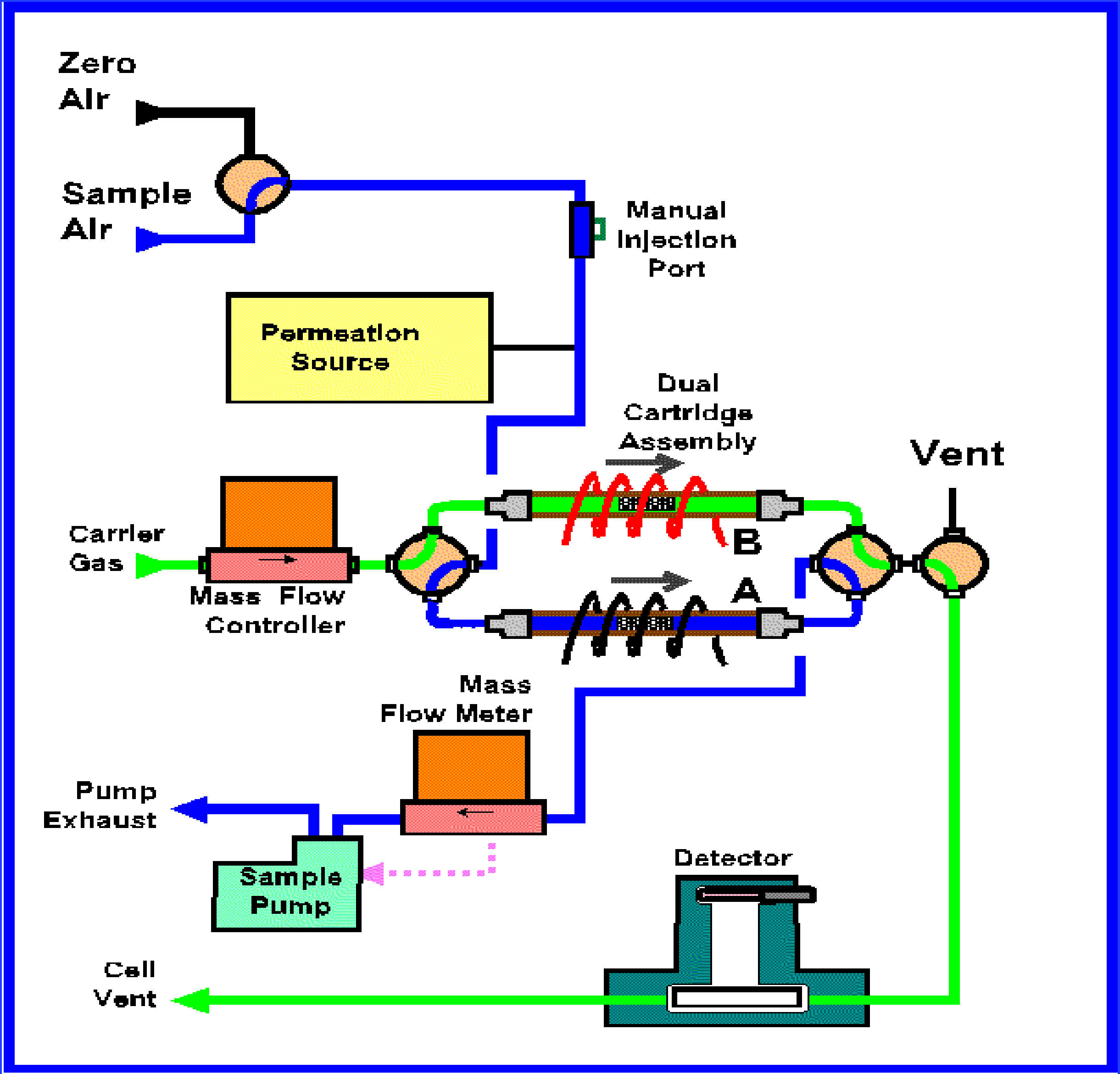
TORERO Hg Objectives

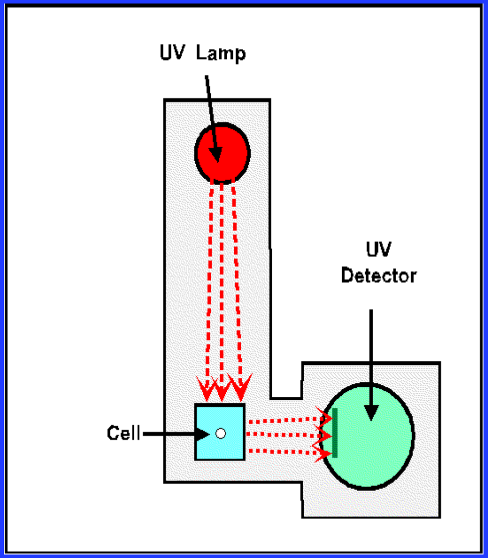
- Measure RGM at a variety of altitudes
- Look for evidence of halogen initiated oxidation of GEM

Approach:

- Sample on KCl coated annular denuders
- Standard operating procedure is to sample at 10 SLPM
- During TORERO we were limited to 10 LPM volumetric so low mass sampling at high altitudes
- Most flights: 5 samples, 2 blanks, 1bypass
- Denuders analyzed immediately post flight using Tekran 2537A Hg analyzer (gold amalgamation / CVAFS)
- Mass flow calculated by integrating flight pressure / temperature profile

CVAFS instrument with presampling on gold (TEKRAN)





CVAFS instrument with presampling on gold

Preconcentrate to enhance sensitivity

Remove very efficient quenching gases N_2 and O_2

Monitor resonance fluorescence in inefficient quencher (Ar)

Annular Denuder Methodology for the Measurement of RGM

***Environ. Sci. Technol.*, 36 (13), 3000 -3009, 2002**

Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air

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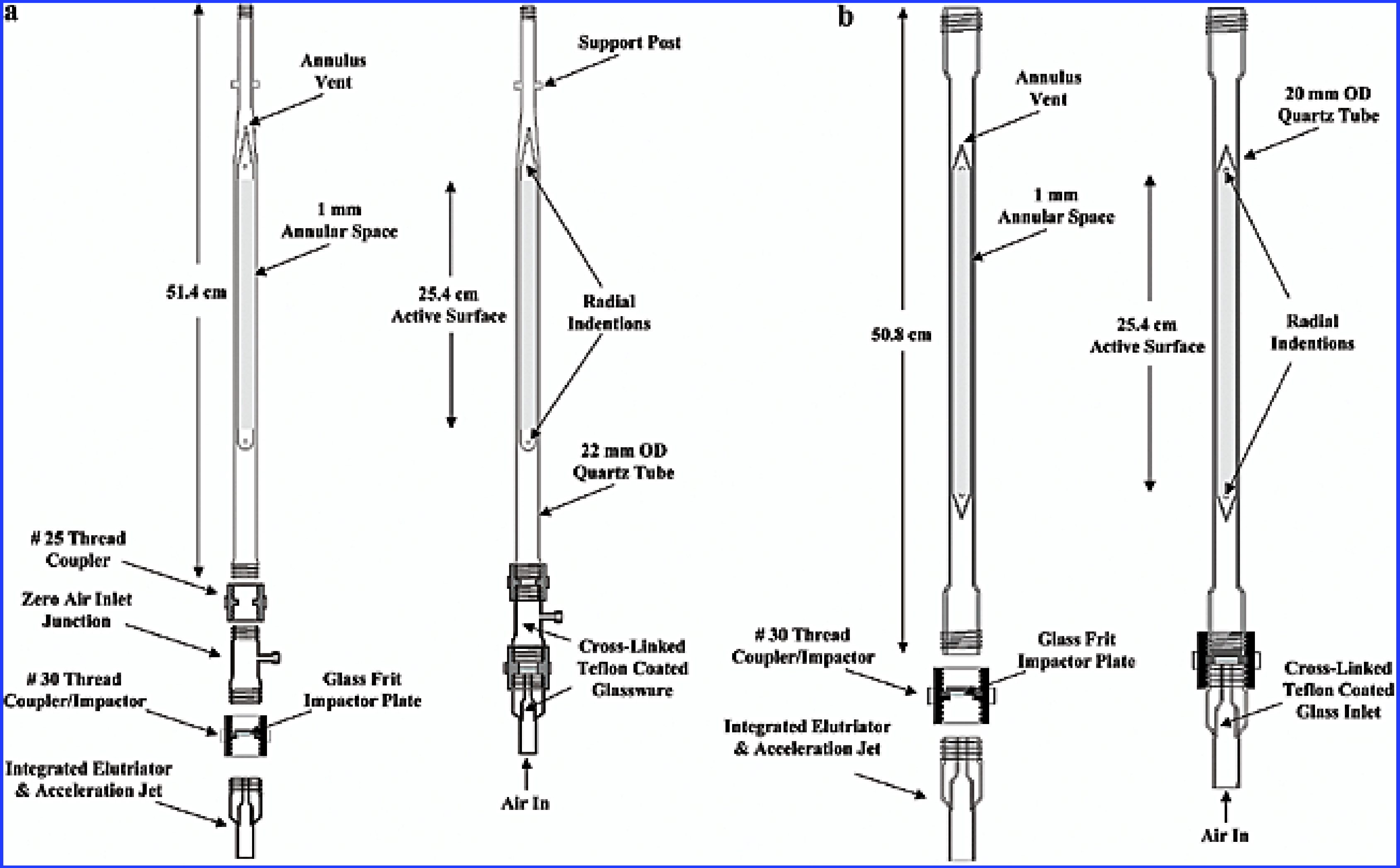
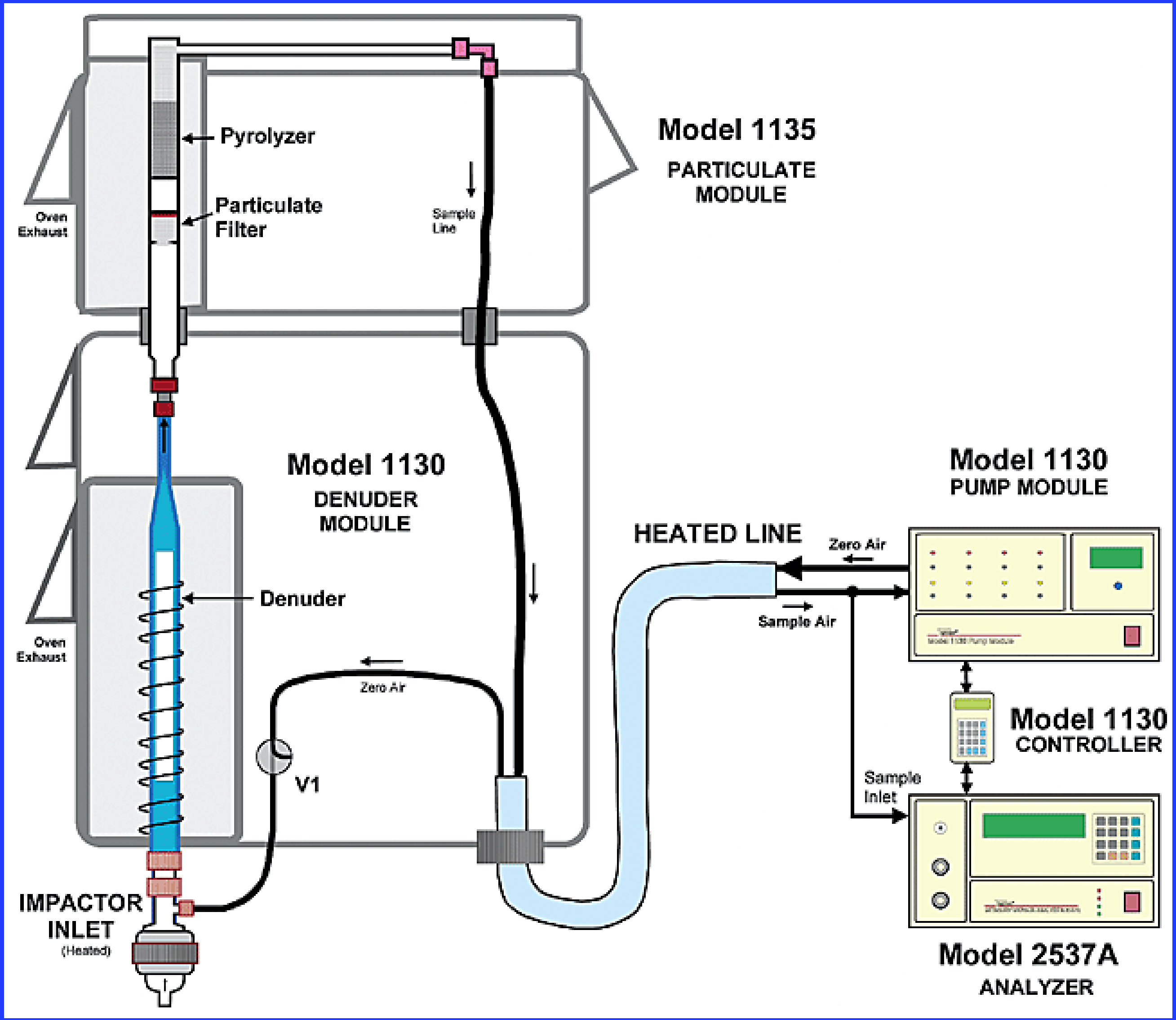


Diagrams of disassembled and assembled quartz annular denuder systems for (a) automated and (b) manual methods, respectively.



Schematic diagram of Tekran automated mercury speciation instrumentation showing the configuration of the model 1130 denuder module and the model 1135 particulate mercury unit.

Research Flight 12: blank: 22 pg

		Average height	vol (Std m^3)	Denuder load	pg/m^3	pg/ Std m^3	2 sig error
1…..	high 35-38K	37796	0.07	9.88	-24.52	-160.38	79.4
2…..	low 0.3-19K	11587	0.54	23.48	1.87	2.95	19.2
3…..	high 43-44K	42746	0.05	16.41	-12.19	-105.28	104.8
4…..	high 44-45.5K	44715	0.05	57.31	78.71	679.80	104.8
5…..	low 0.3-23K	10139	0.62	38.47	17.83	26.34	17.9

Research Flight 13: blank: 6 pg

		Average height	vol (Std m^3)	Denuder load	pg/m3	pg/ Std m3	2 sig error
1	D 7 high	34910	0.09	4.72	-3.33	-17.76	18.7
2	D 6 high	39931	0.07	14.46	15.38	114.00	25.9
3	D 5 high	44806	0.04	5.76	-1.37	-13.32	34.0
4	D 3 high	45521	0.04	8.36	4.71	51.87	35.5
5	D 2 high	46524	0.03	5.50	-2.38	-25.67	37.8

Research Flight 14: blank: 6 pg

		Average height	vol (Std m^3)	Denuder load	pg/m3	pg/ Std m3	2 sig error
1	D 2 high	39819	0.16	18.82	10.69	78.61	25.7
2	D 3 low	10384	0.36	39.38	59.04	90.91	5.4
3	D 5 high	44595	0.05	9.24	5.75	55.31	33.7
4	D 7 high	47246	0.04	6.21	-0.22	-2.37	38.3

Research Flight 15: blank: 6 pg

		Average height	vol (Std m³)	Denuder load	pg/m3	pg/Std m3	2 sig error
1	D 5 high	38466	0.09	18.19	19.79	135.11	23.9
2	D2 6000-26000	14931	0.33	33.08	43.53	80.78	6.5
3	D 3 300-5000	1063	0.91	49.48	45.44	47.39	3.6
4	D 6 high	44697	0.12	12.79	5.81	56.11	33.8
5	D 7 high	47528	0.05	11.56	10.10	114.41	39.6

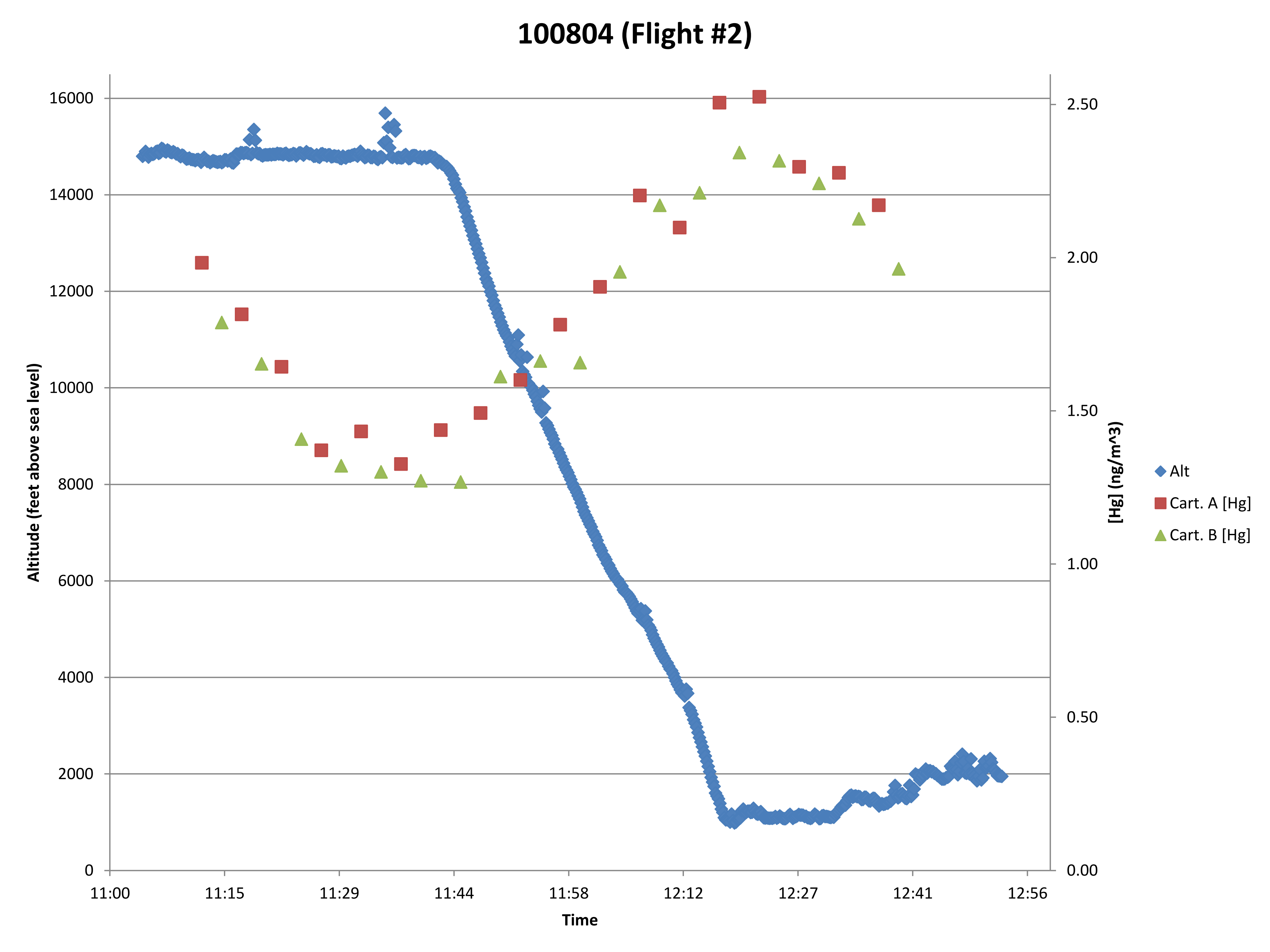
Research Flight 16: blank: 6 pg

		Average height	vol (Std m^3)	Denuder load	pg/m3	pg/Std m3	2 sig error
1	D 2 < 7000ft	2563	0.5	27.46	38.49	42.55	3.9
2	D 3 300-5000	1544	0.59	45.42	62.94	66.83	3.7
3	D 5 >40000	43658	0.07	17.54	18.42	167.13	31.7
4	D 7 40-45Kft	47091	0.05	14.92	16.25	179.40	38.6
5	D 6 6-26Kft	19162	0.1	12.28	25.80	59.10	8.0

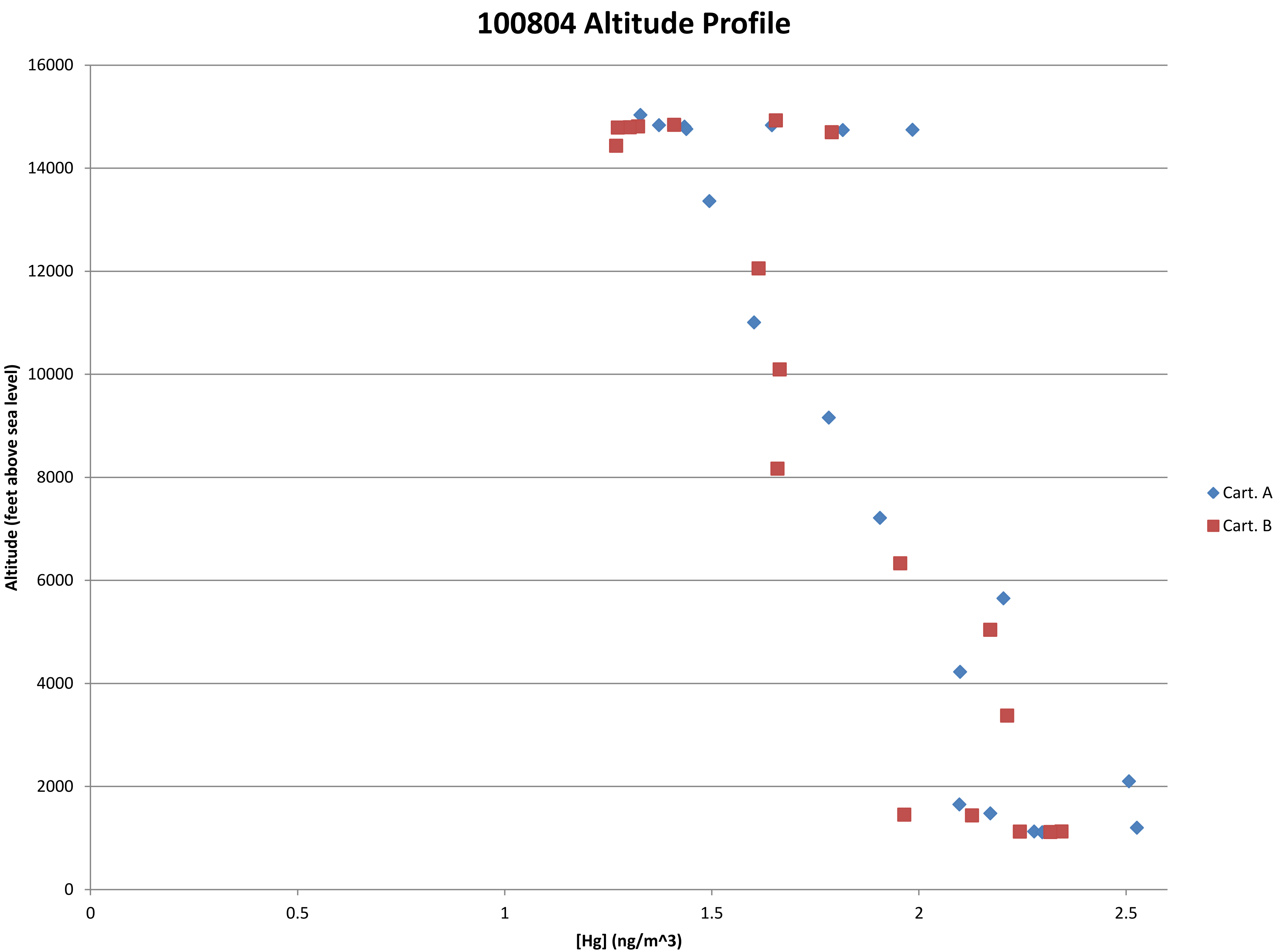
Research Flight 17: blank: 6 pg

		Average height	vol (Std m^3)	Denuder load	pg/m3	pg/Std m3	2 sig error
1	D 5 33000	33500	0.10	17.20	21.77	110.83	17.8
2	D 2 6k-26kft	11685	0.22	15.43	28.48	45.48	5.6
3	D 3 300-5000	1102	0.32	21.76	45.44	47.34	3.6
4	plumbing	problem	:	bypass	partially	open	
5	D 7 40-45Kft	41260	0.04	8.55	7.71	59.79	27.1

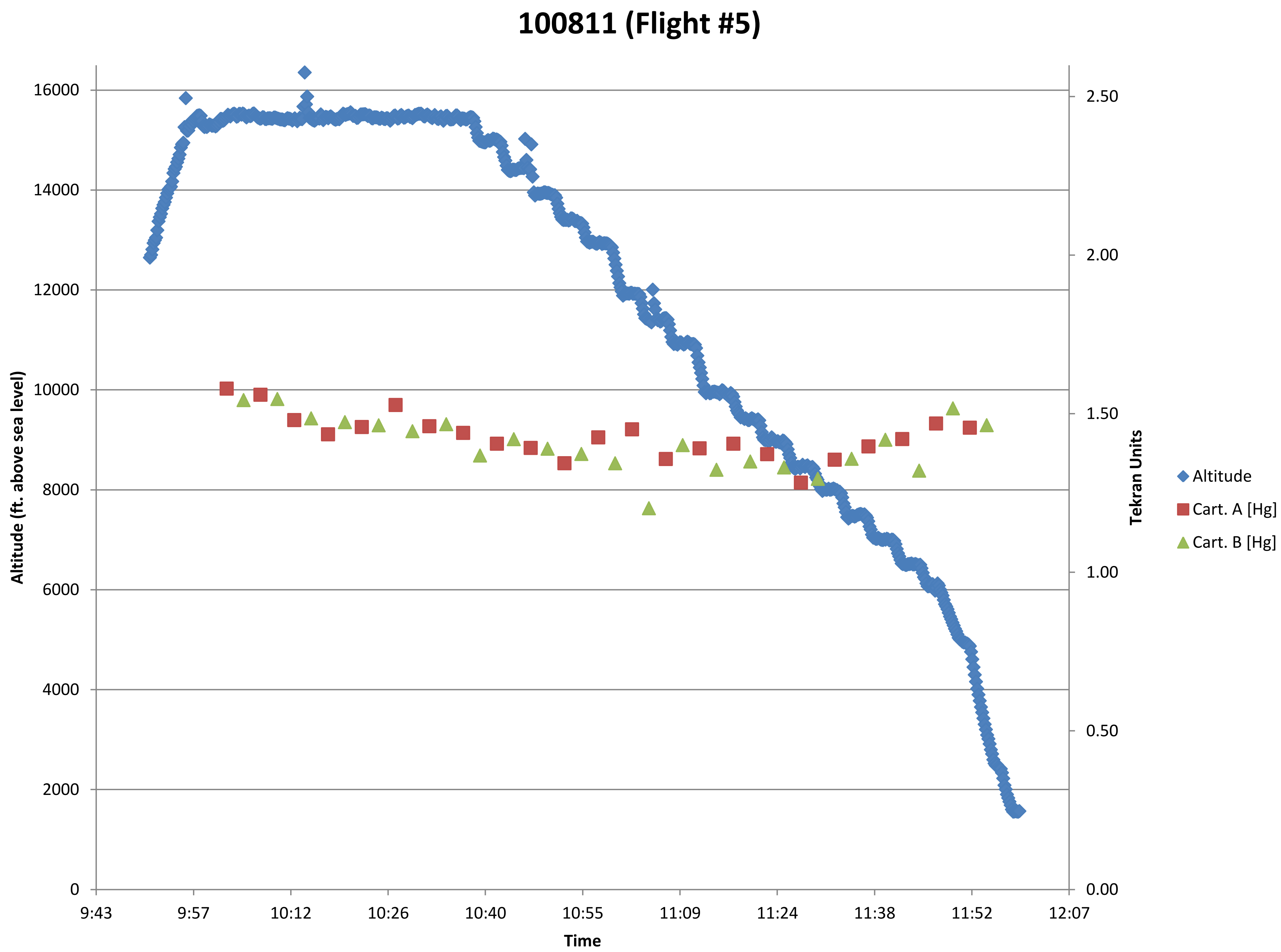
Airborne Hg Sampling in Grand Bay, MS

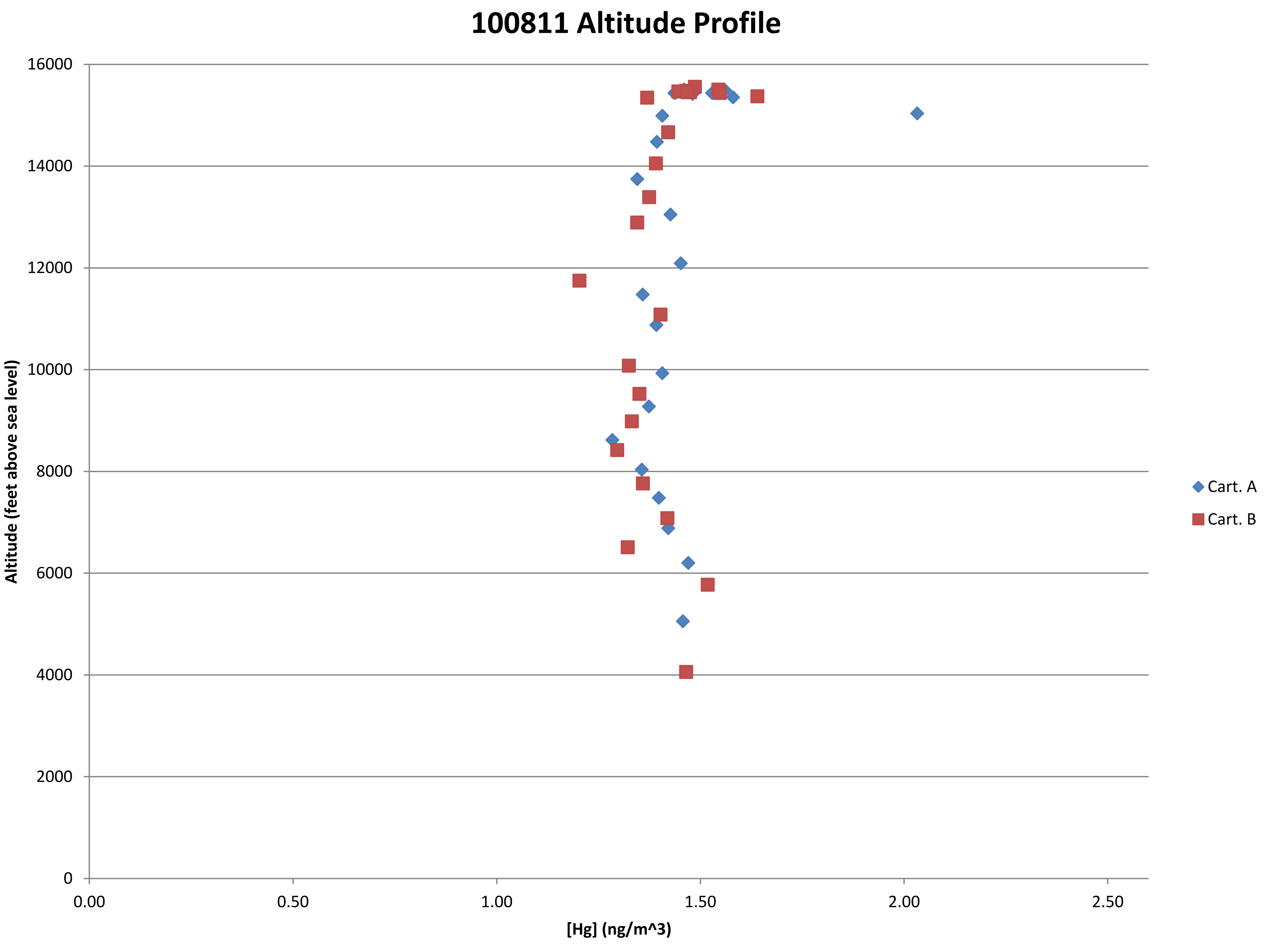


100804 (Flight #2)
Altitude (feet above sea level)
16000
14000
12000
10000
8000
6000
4000
2000
0
[Hg] (ng/m^3)
2.50
2.00
1.50
1.00
0.50
0.00
Time
11:00
11:15
11:29
11:44
11:58
12:12
12:27
12:41
12:56
Alt
Cart. A [Hg]
Cart. B [Hg]

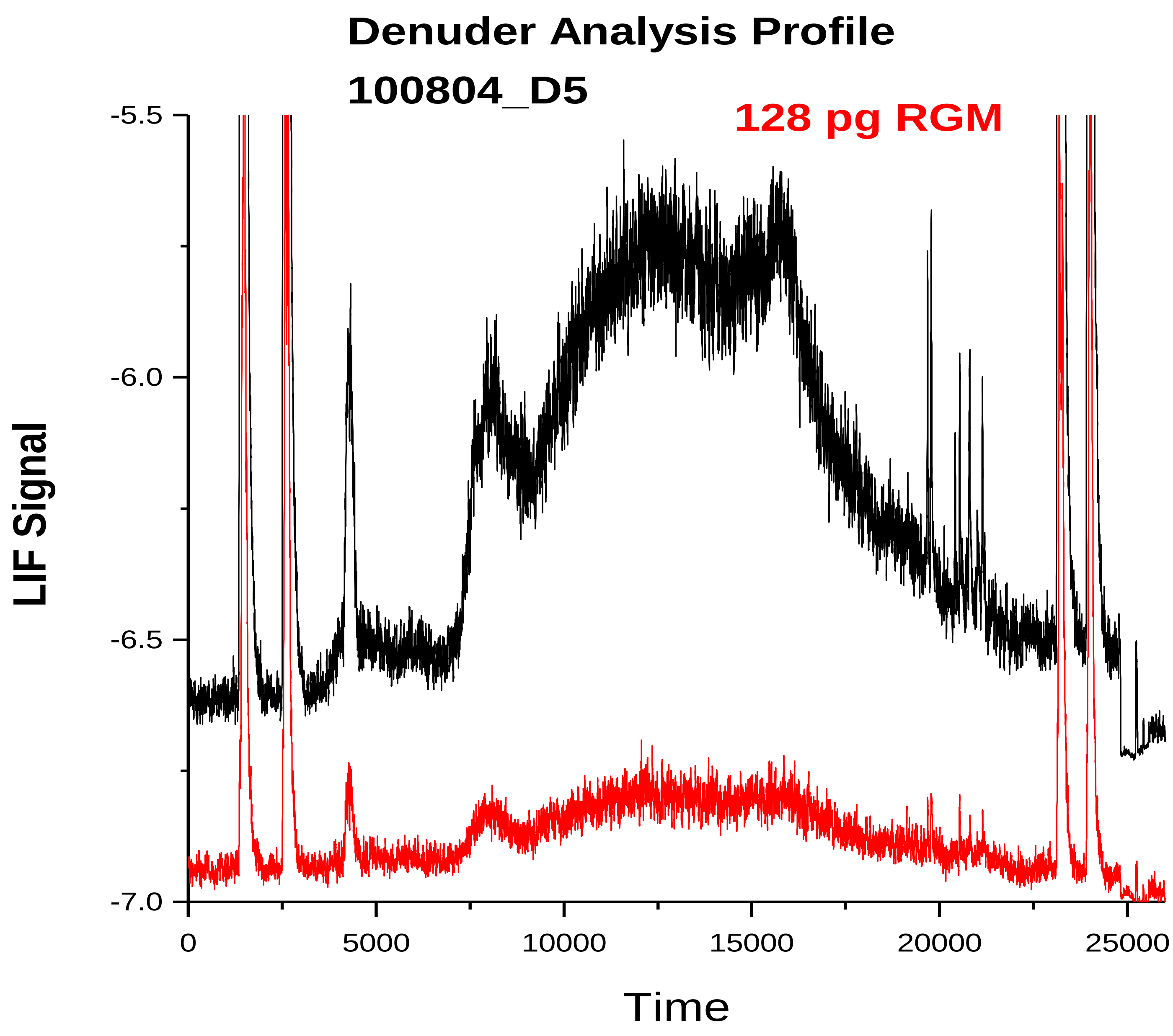


100804 Altitude Profile
16000
14000
12000
10000
8000
6000
4000
2000
0
0
0.5
1
1.5
2
2.5
Altitude (feet above sea level)
[Hg] (ng/m^3)
Cart. A
Cart. B

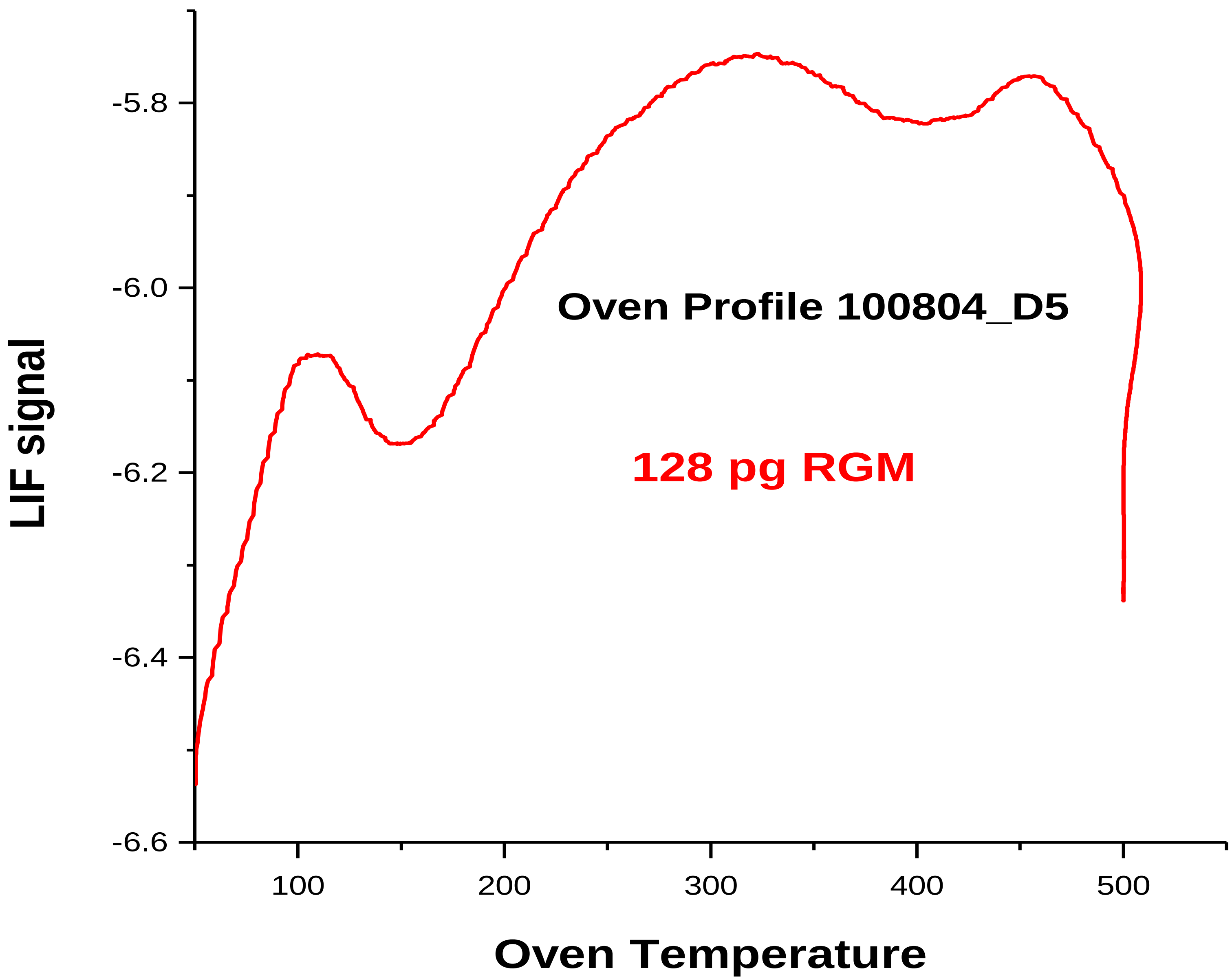

100811 (Flight #5)
Altitude (ft. above sea level)
16000
14000
12000
10000
8000
6000
4000
2000
0
Tekran Units
2.50
2.00
1.50
1.00
0.50
0.00
9:43
9:57
10:12
10:26
10:40
10:55
11:09
11:24
11:38
11:52
12:07
Time
Altitude
Cart. A [Hg]
Cart. B [Hg]

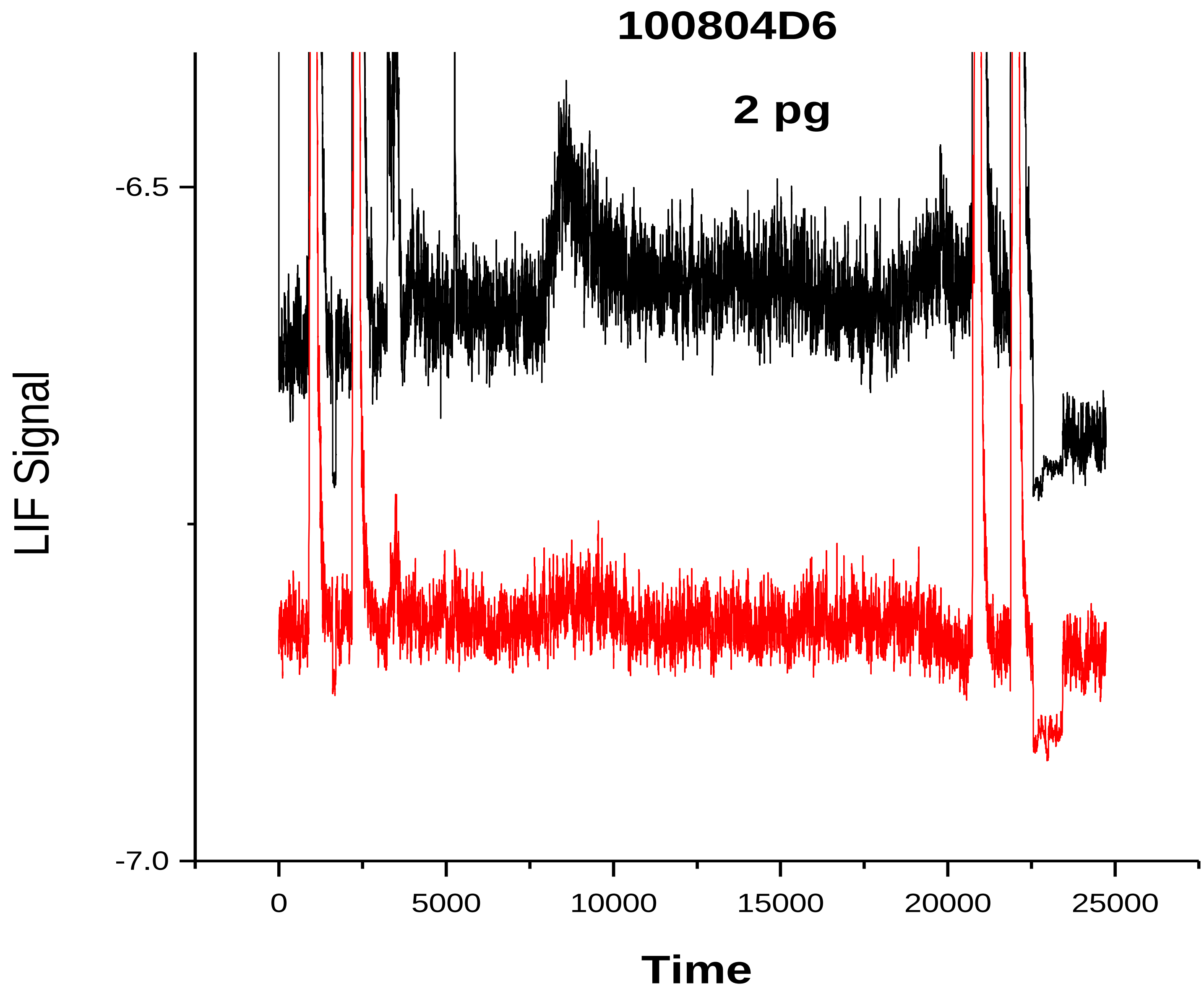


100811 Altitude Profile
16000
14000
12000
10000
8000
6000
4000
2000
0
Altitude (feet above sea level)
0.00
0.50
1.00
1.50
2.00
2.50
[Hg] (ng/m^3)
Cart. A
Cart. B

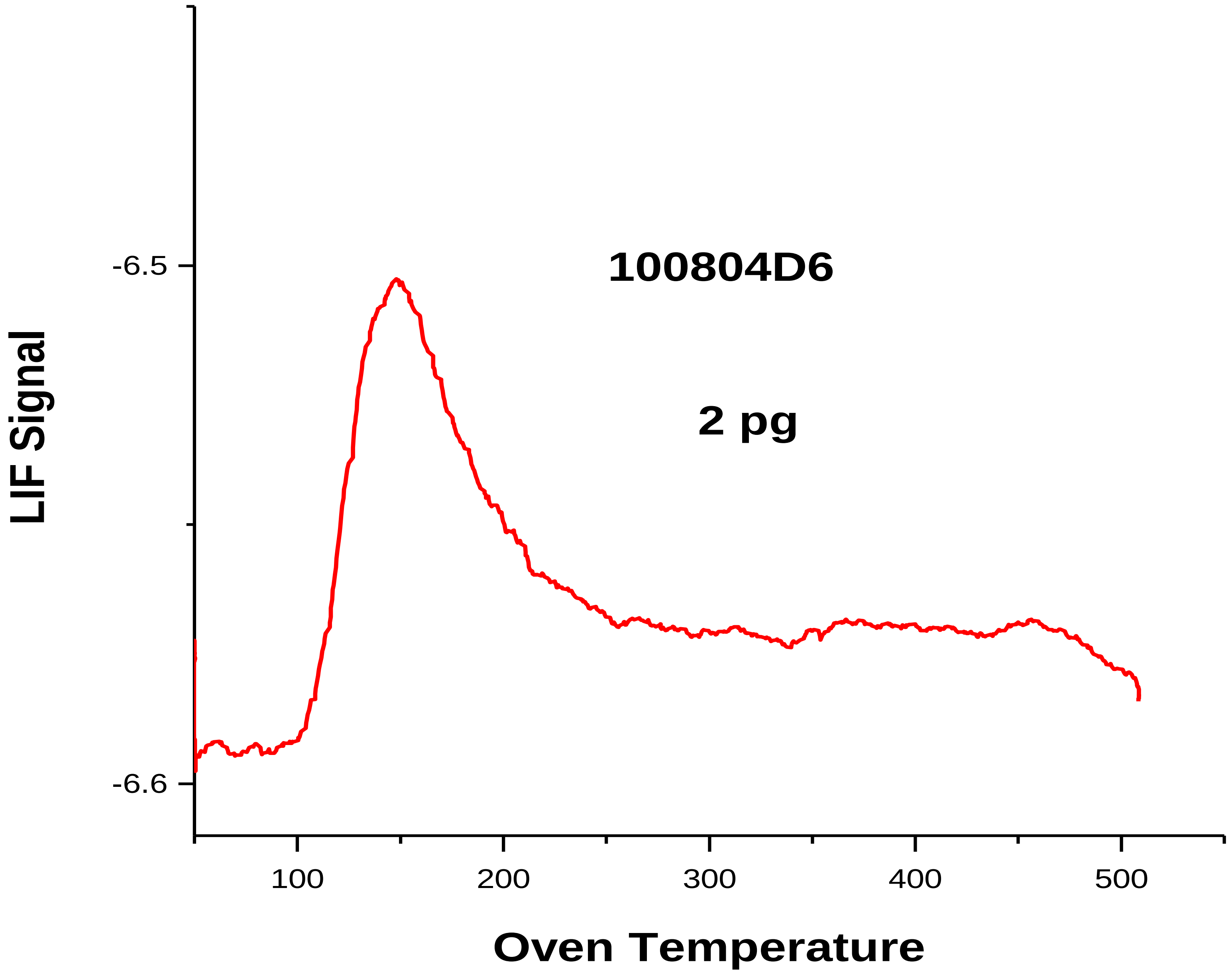


Denuder Analysis Profile
100804_D5
128 pg RGM
LIF Signal
-5.5
-6.0
-6.5
-7.0
0
5000
10000
15000
20000
25000
Time

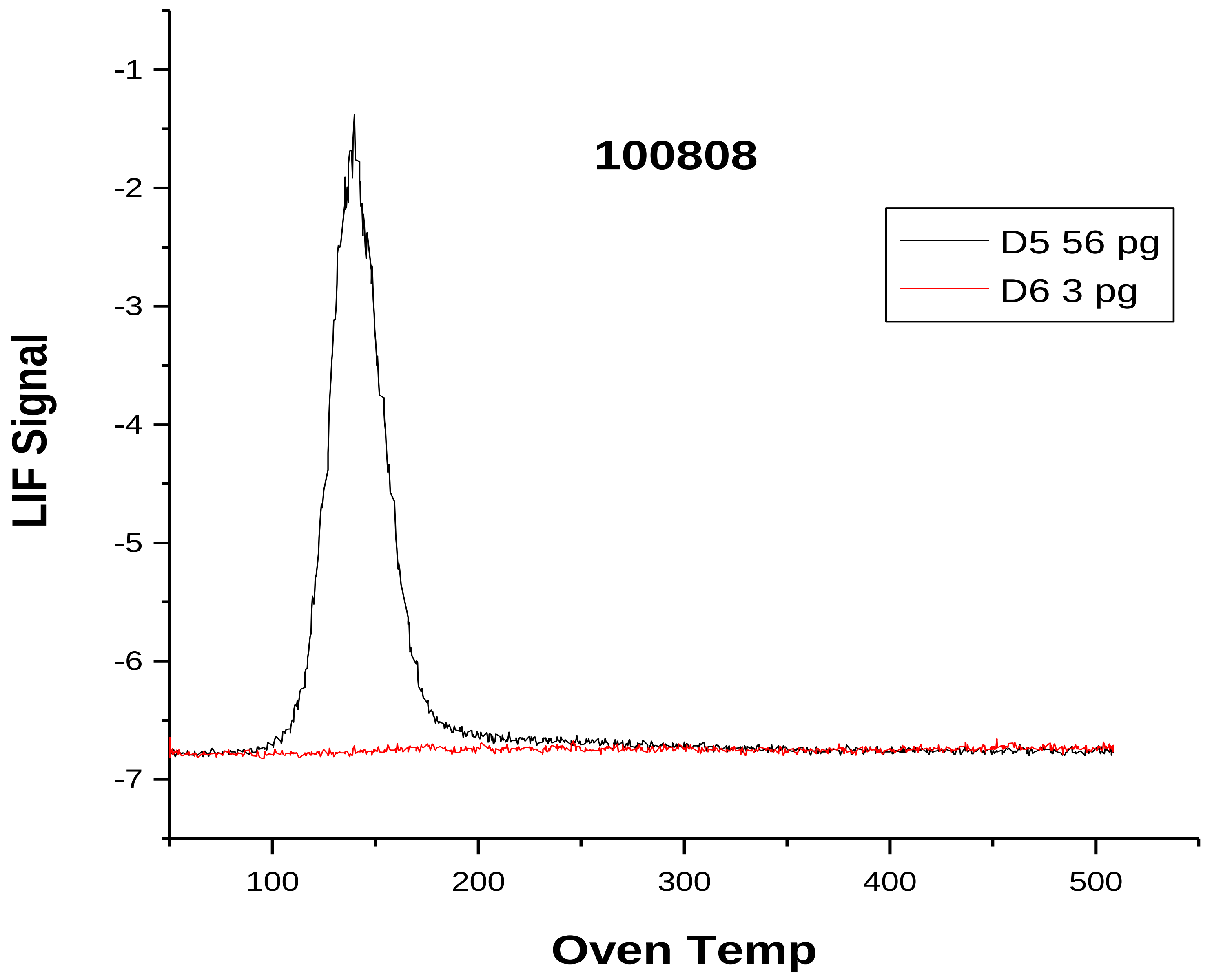

Oven Profile 100804_D5
128 pg RGM
LIF signal
-5.8
-6.0
-6.2
-6.4
-6.6
100
200
300
400
500
Oven Temperature



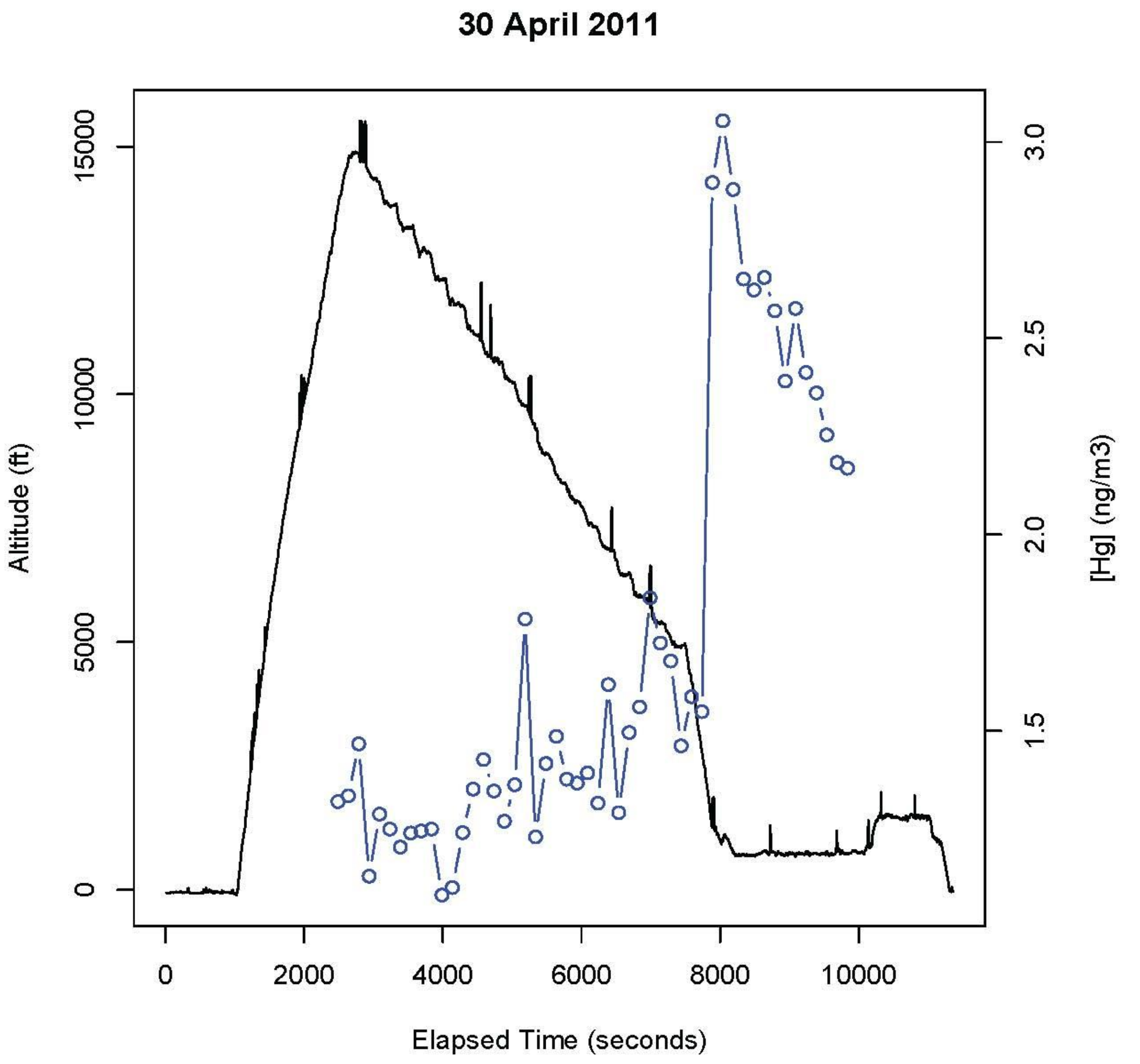
100804D6
2 pg
-6.5
-7.0
LIF Signal
0
5000
10000
15000
20000
25000
Time



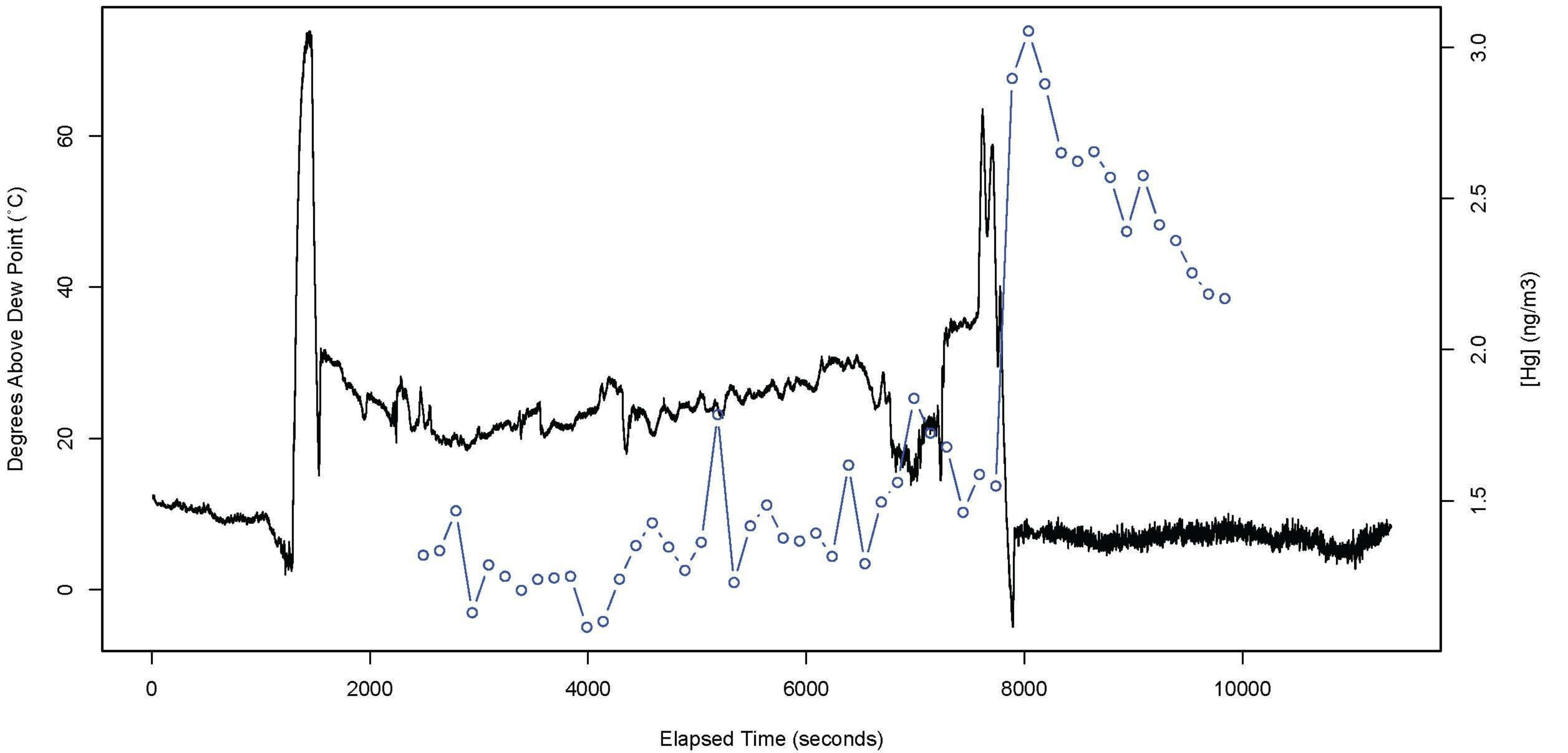
100804D6
2 pg
LIF Signal
-6.5
-6.6
100
200
300
400
500
Oven Temperature

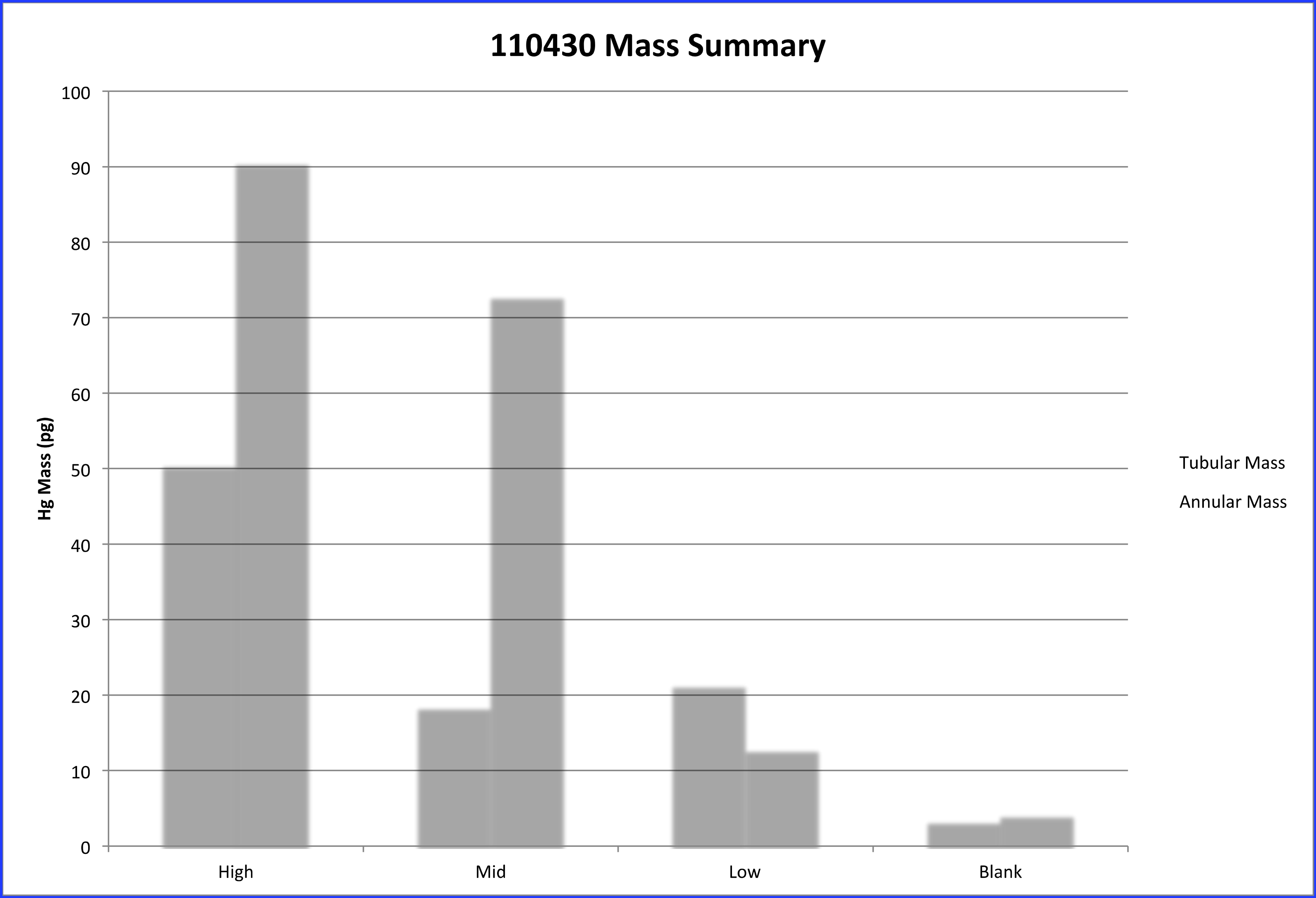


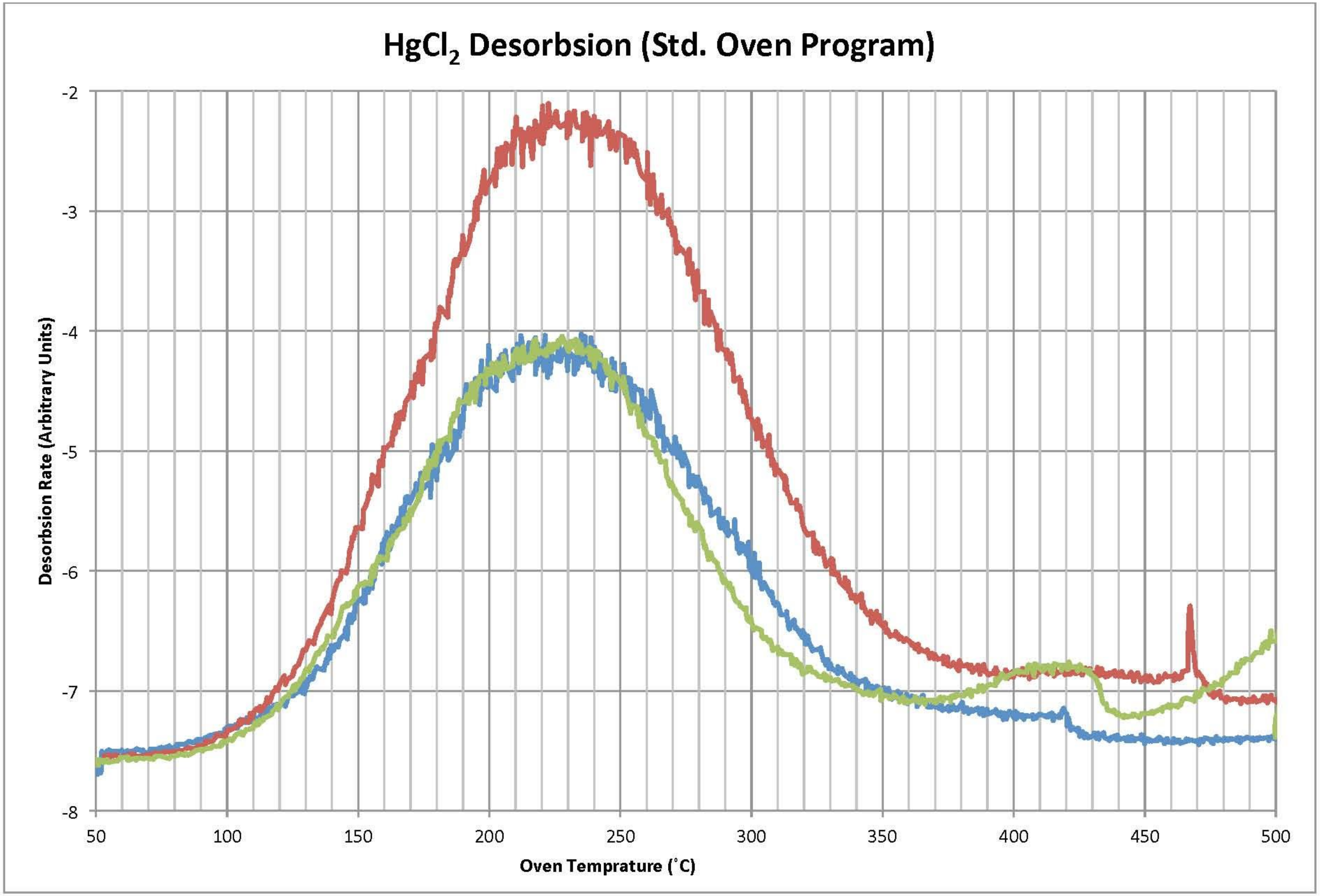
100808
D5 56 pg
D6 3 pg
LIF Signal
-1
-2
-3
-4
-5
-6
-7
100
200
300
400
500
Oven Temp


30 April 2011
Altitude (ft)
0
5000
10000
15000
[Hg] (ng/m3)
1.5
2.0
2.5
3.0
0
2000
4000
6000
8000
10000
Elapsed Time (seconds)

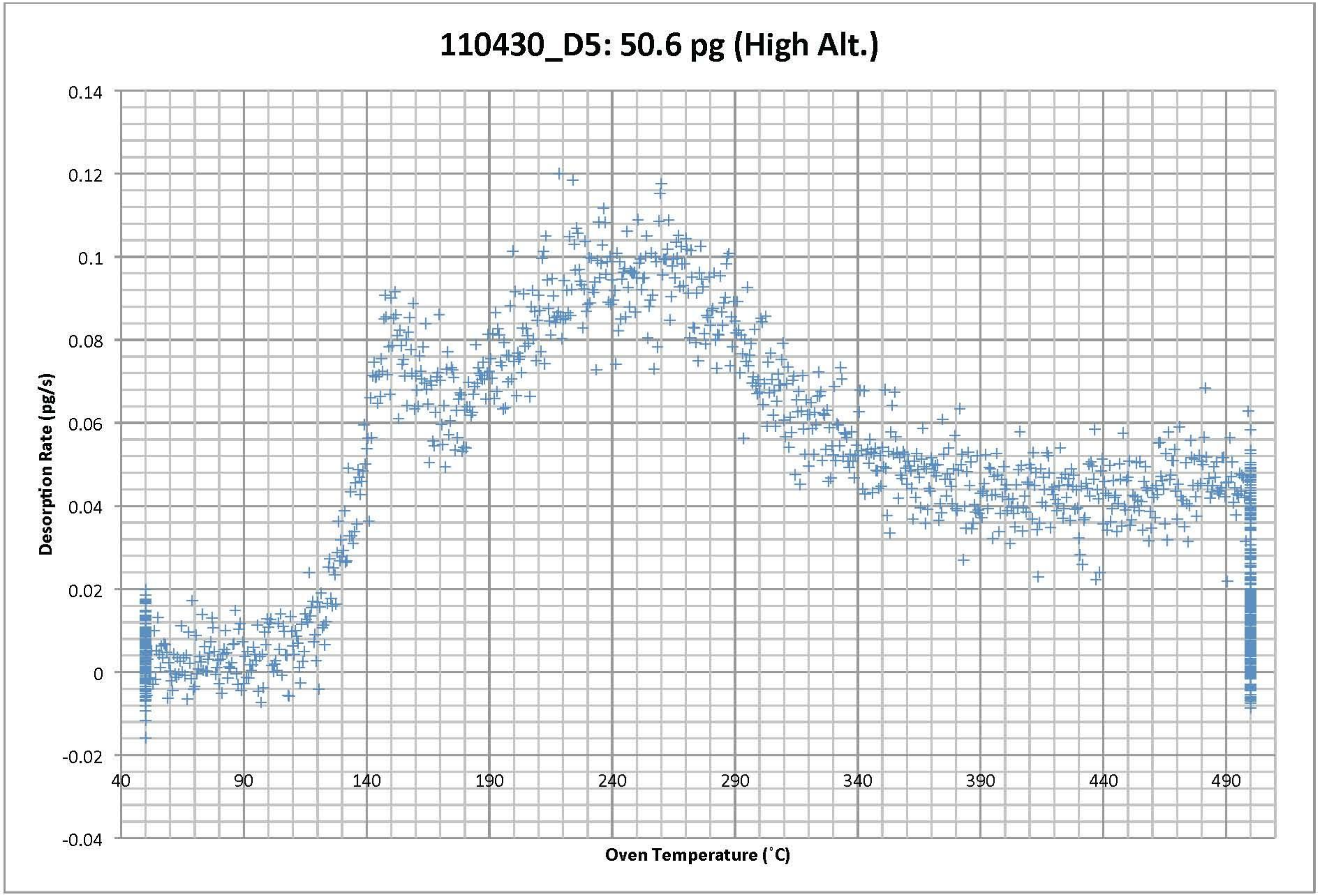
Flight #4: 30 August 2011



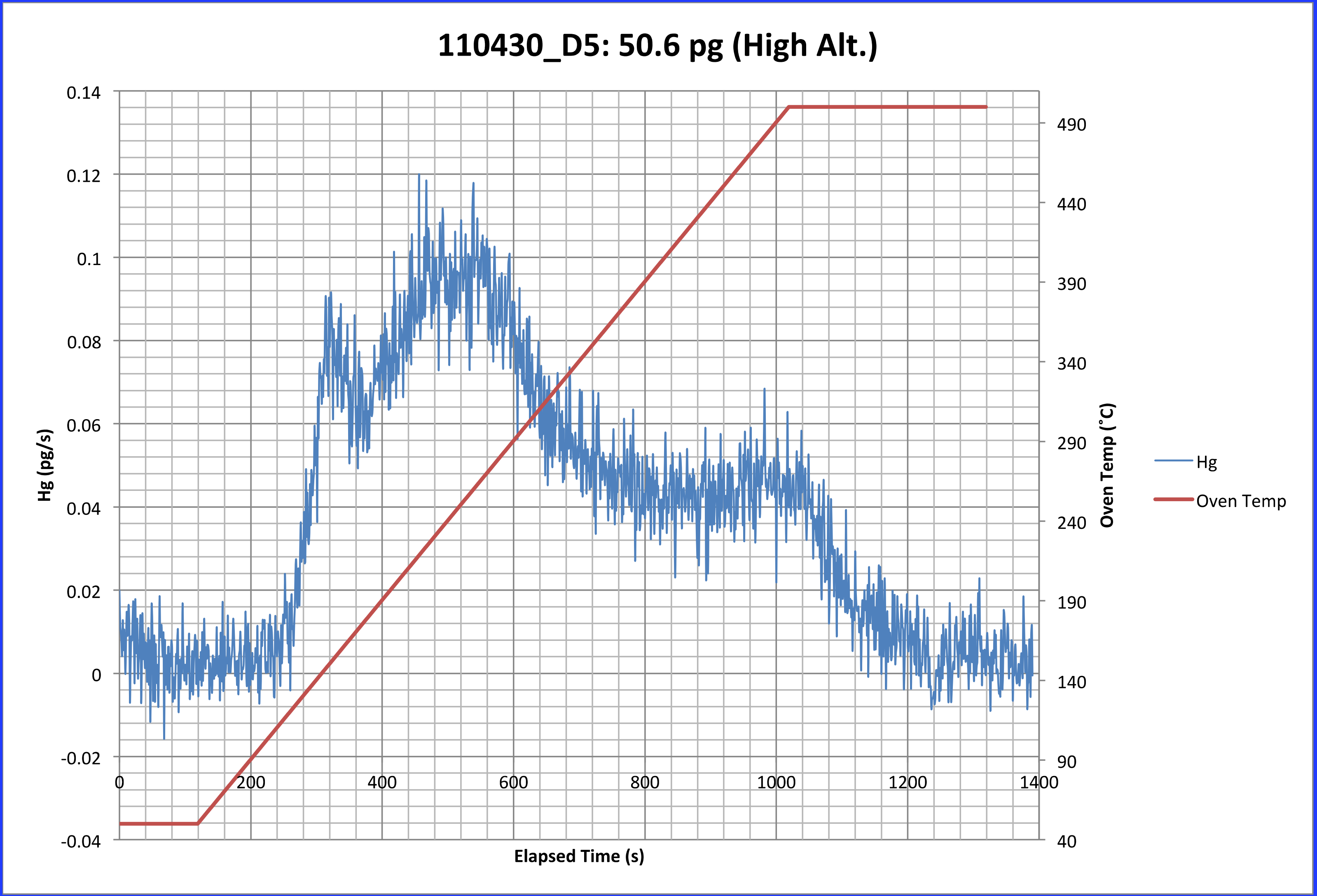

110430 Mass Summary
Hg Mass (pg)
100
90
80
70
60
50
40
30
20
10
0
High
Mid
Low
Blank
Tubular Mass
Annular Mass



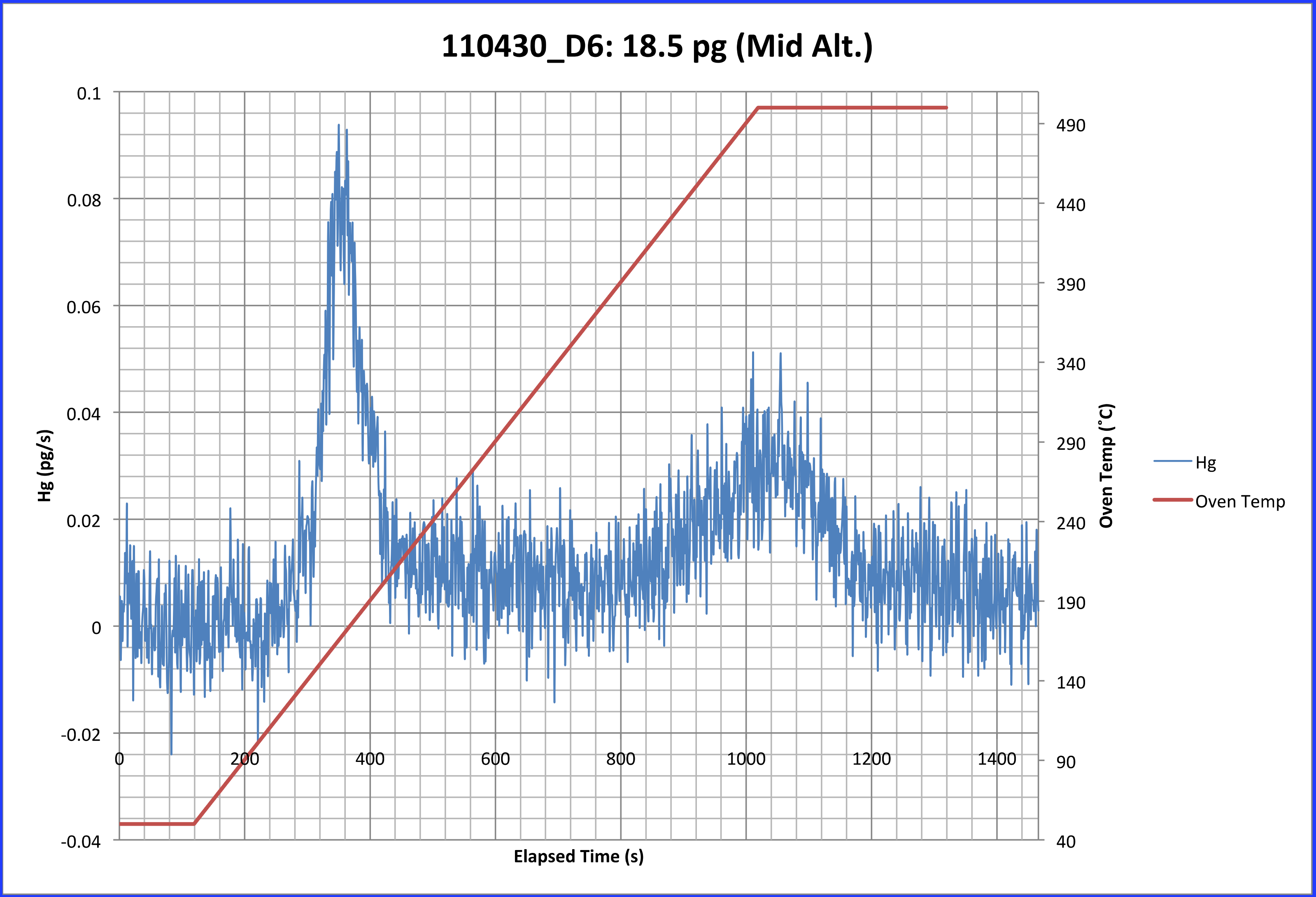
HgCl2 Desorbsion (Std. Oven Program)
-2
-3
-4
-5
-6
-7
-8
Desorbsion Rate (Arbitrary Units)
50
100
150
200
250
300
350
400
450
500
Oven Temprature (˚C)



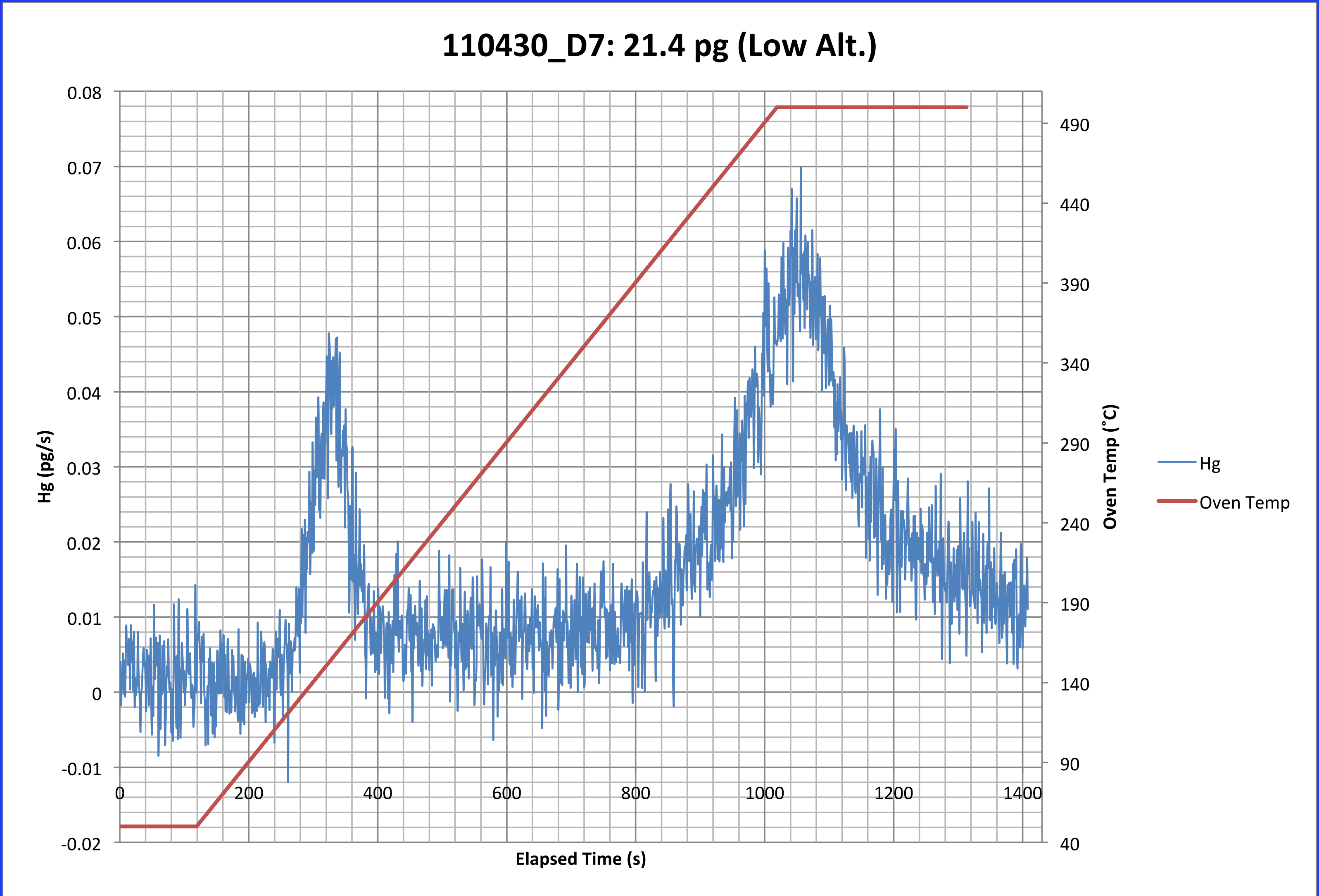
110430_D5: 50.6 pg (High Alt.)
Desorption Rate (pg/s)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
40
90
140
190
240
290
340
390
440
490
Oven Temperature (˚C)

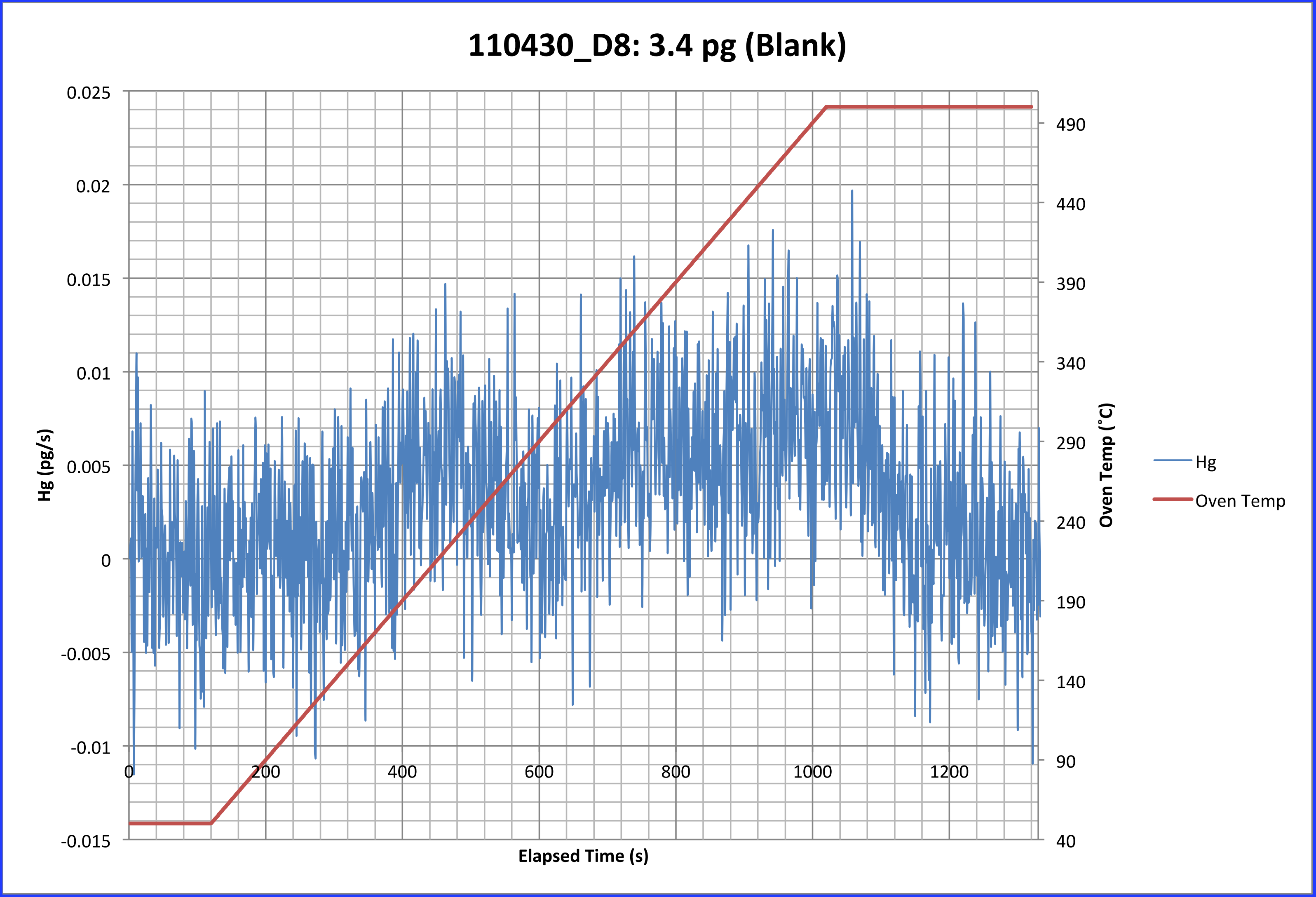


110430_D5: 50.6 pg (High Alt.)
Hg (pg/s)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
Oven Temp (˚C)
490
440
390
340
290
240
190
140
90
40
0
200
400
600
800
1000
1200
1400
Elapsed Time (s)
Hg
Oven Temp



110430_D6: 18.5 pg (Mid Alt.)
Hg (pg/s)
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
Oven Temp (˚C)
490
440
390
340
290
240
190
140
90
40
0
200
400
600
800
1000
1200
1400
Elapsed Time (s)
Hg
Oven Temp

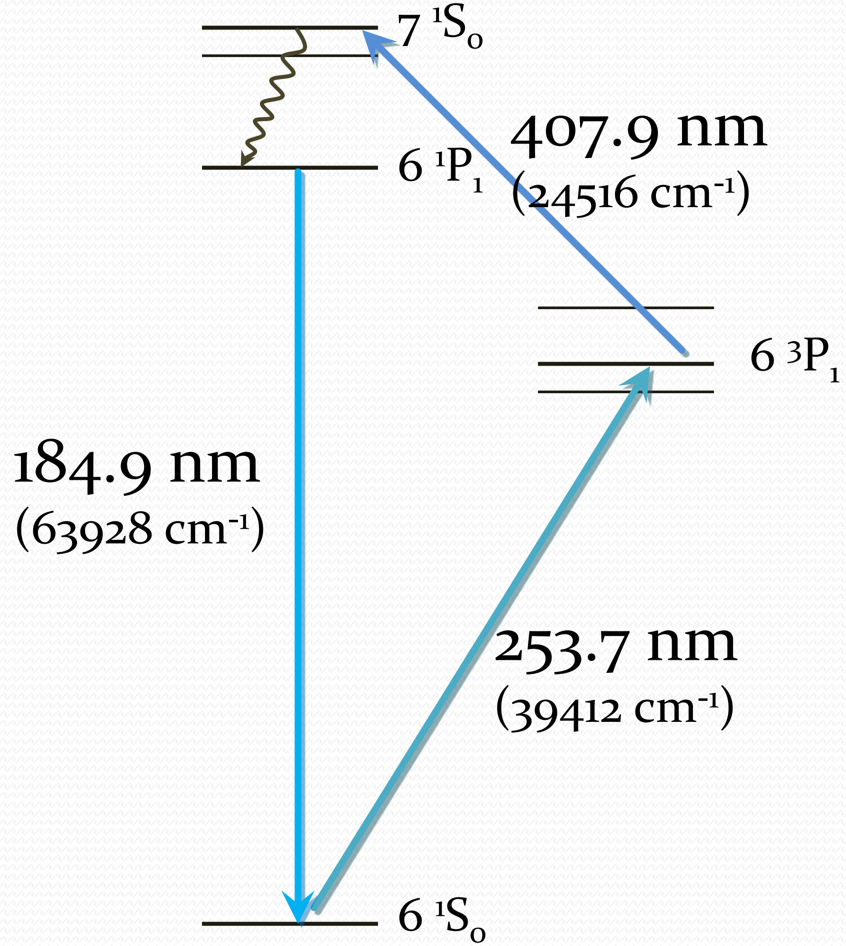

110430_D7: 21.4 pg (Low Alt.)
Hg (pg/s)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
Oven Temp (˚C)
490
440
390
340
290
240
190
140
90
40
0
200
400
600
800
1000
1200
1400
Elapsed Time (s)
Hg
Oven Temp

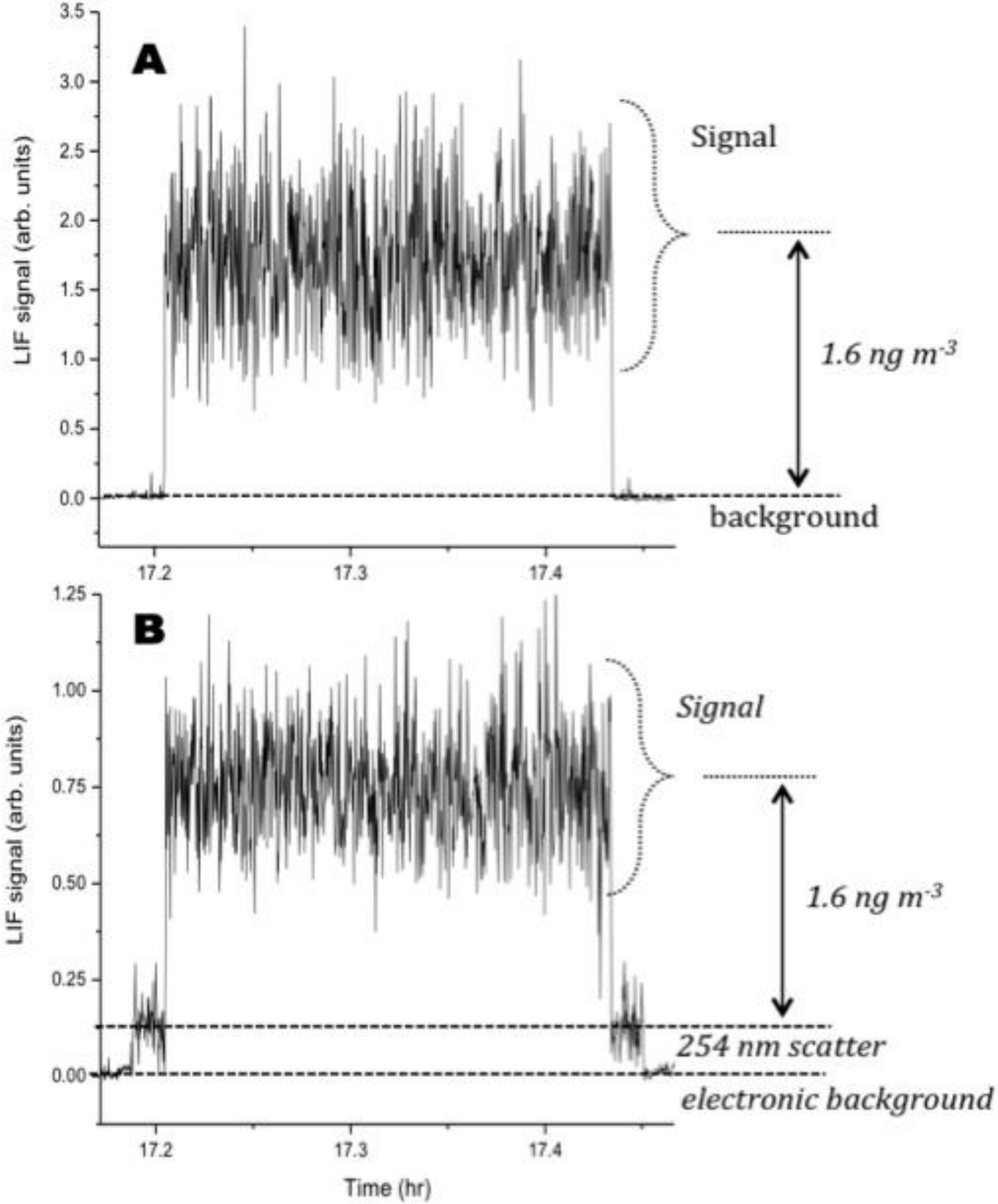


110430_D8: 3.4 pg (Blank)
Hg (pg/s)
0.025
0.02
0.015
0.01
0.005
0
-0.005
-0.01
-0.015
0
200
400
600
800
1000
1200
Elapsed Time (s)
490
440
390
340
290
240
190
140
90
40
Oven Temp (˚C)
Hg
Oven Temp

In-situ measurement of GEM using 2-photon laser-induced fluorescence

- Differentiation between probe lasers and fluorescence signal




A
B
LIF signal (arb. units)
Signal
1.6 ng m-3
background
254 nm scatter
electronic background
Time (hr)
17.2
17.3
17.4

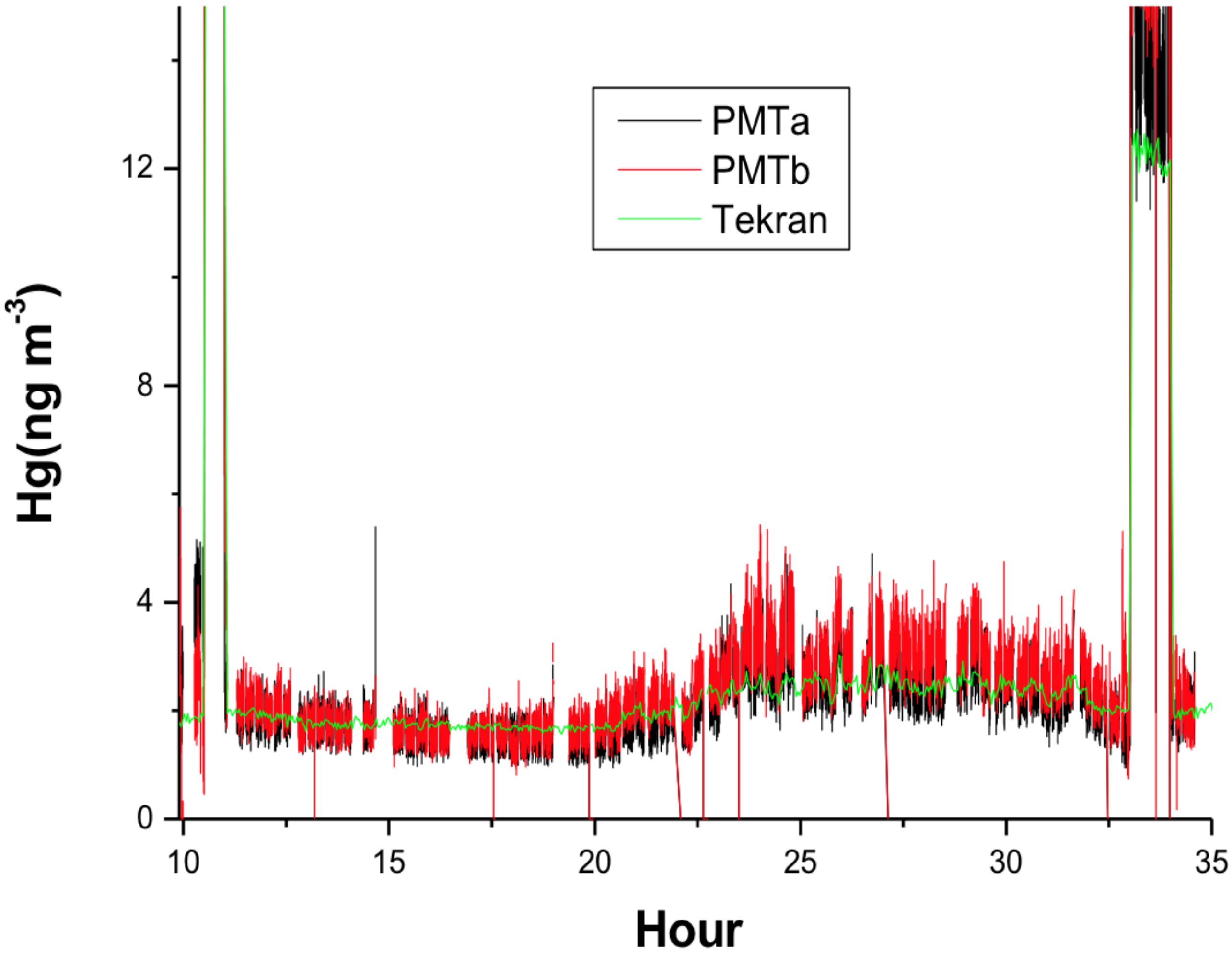


Fig.2 LIF and Tekran signals over a 25 hour sampling period on Sept ½, expanded concentration scale.

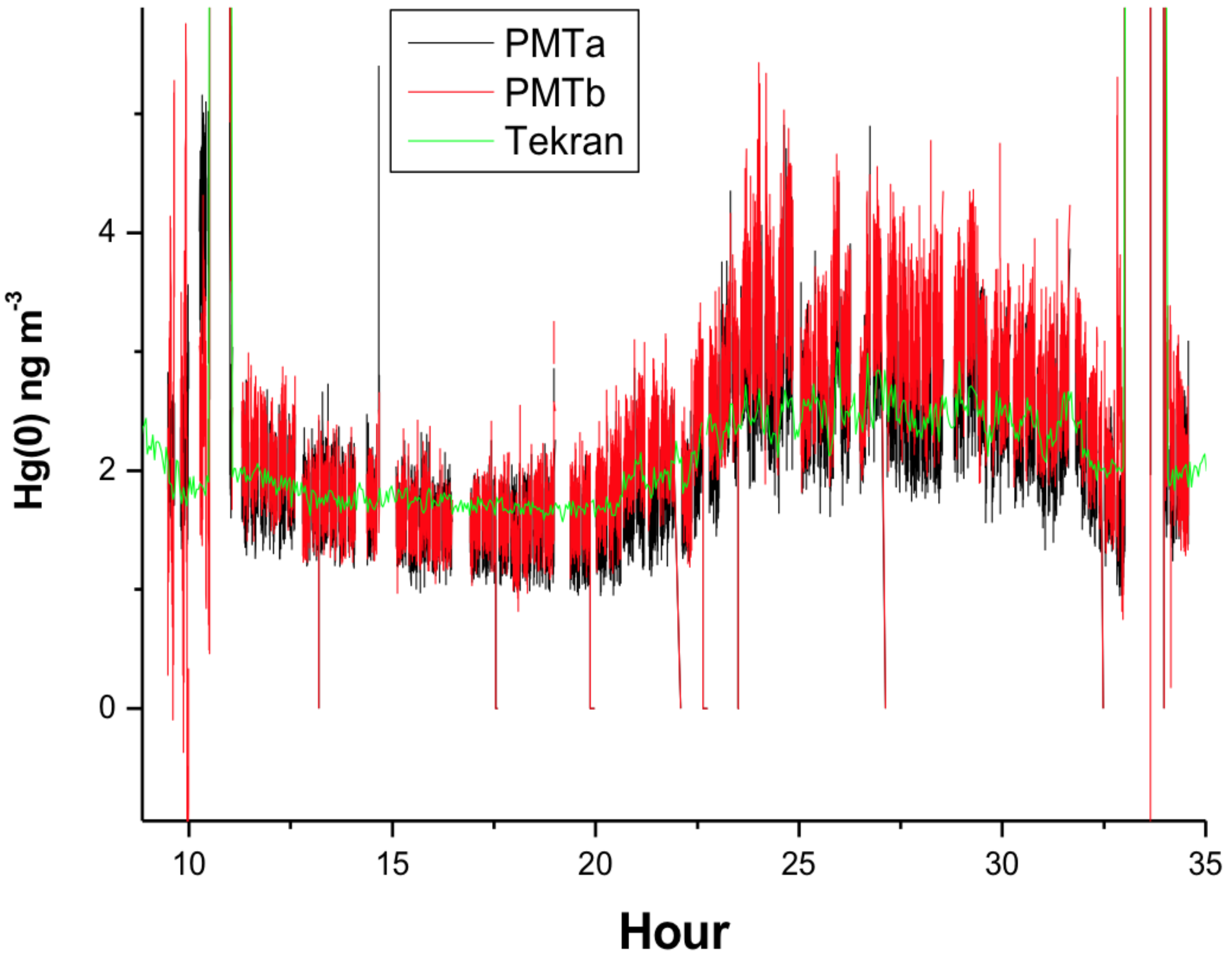
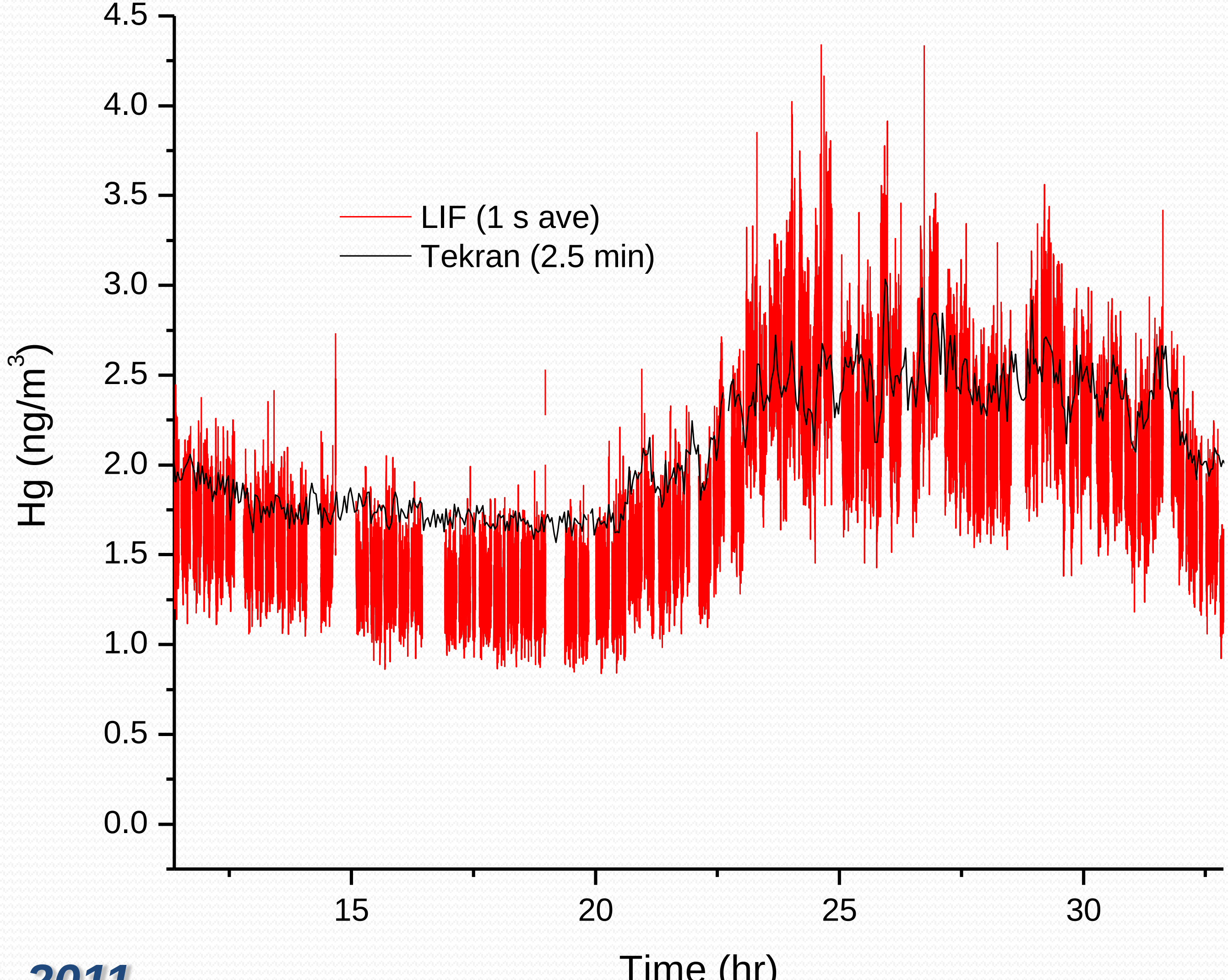


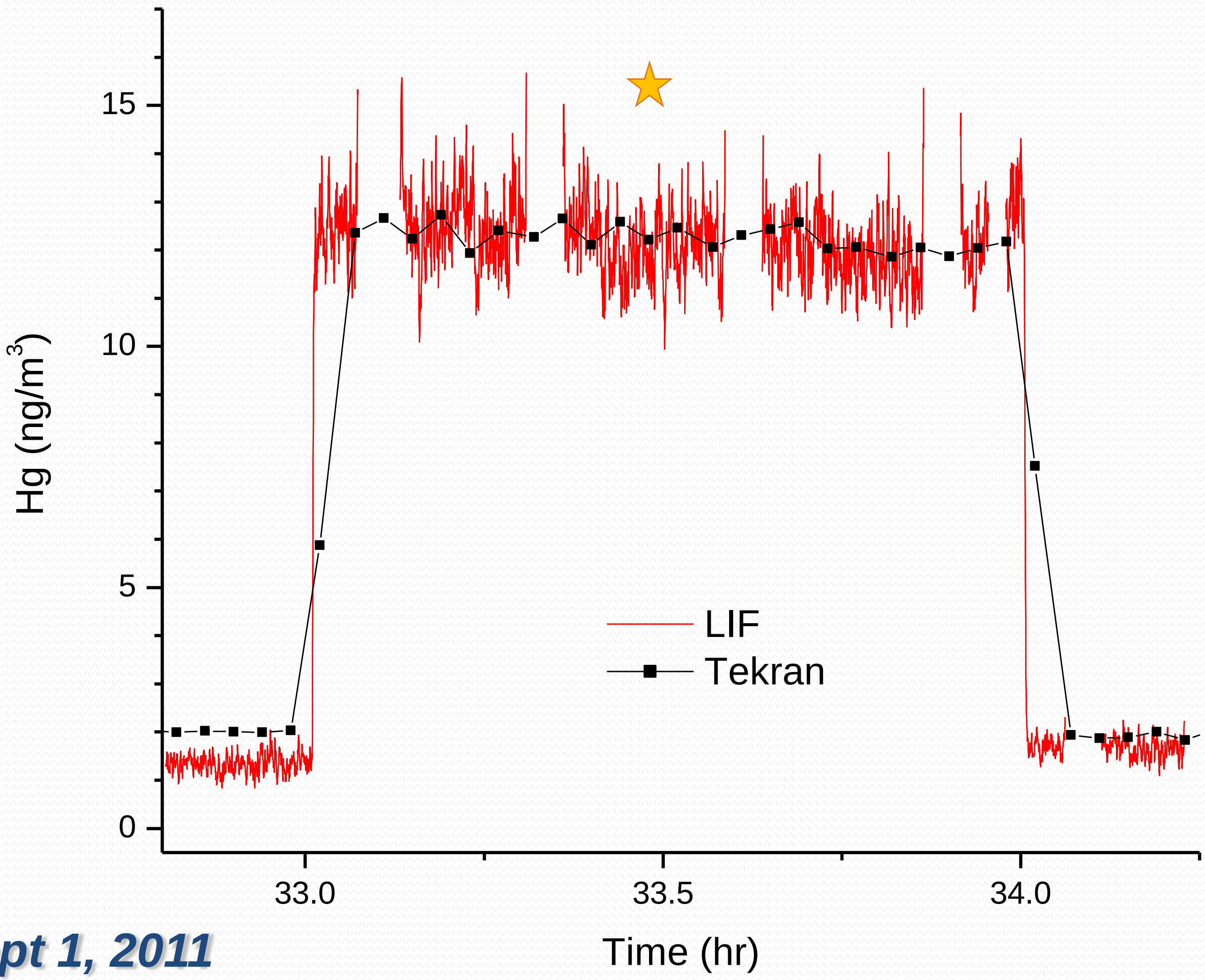
Fig.3 LIF and Tekran signals over a 25 hour sampling period on Sept ½, further expanded concentration scale.

GEM Measurement



Sept 1, 2011

Time Resolution



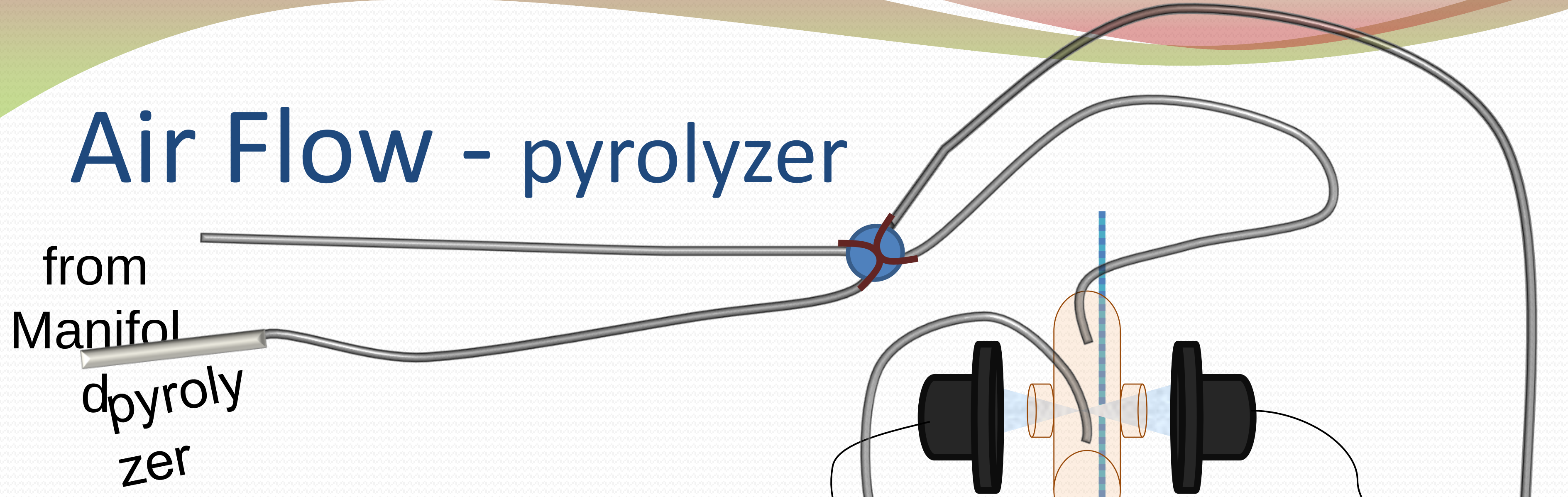
Rise Time

LIF : ≤ 1 s

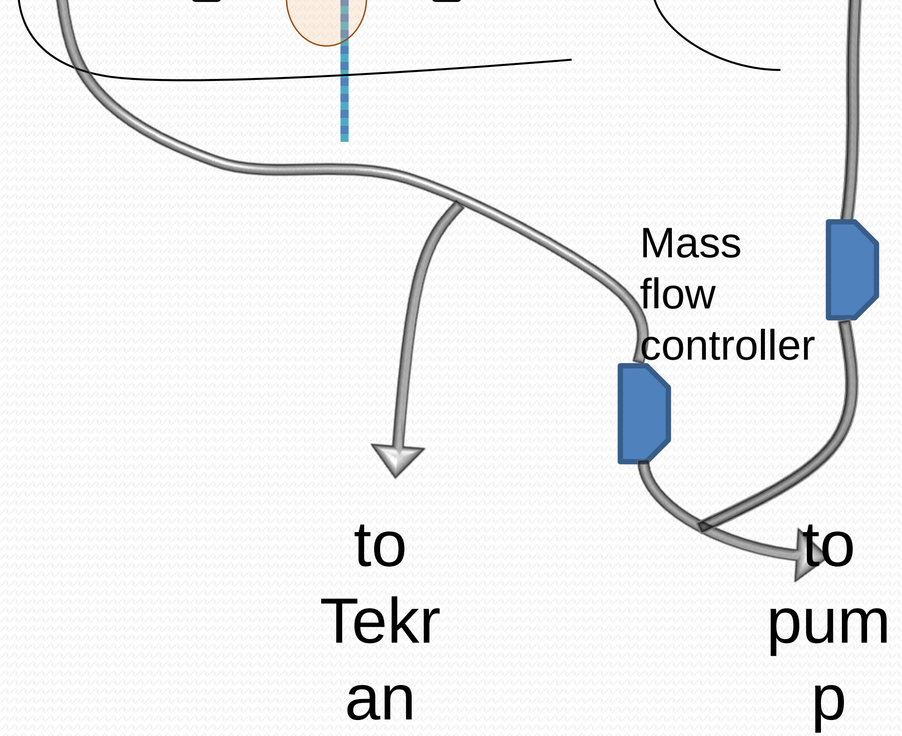
Tekran : 5 min

Sept 1, 2011

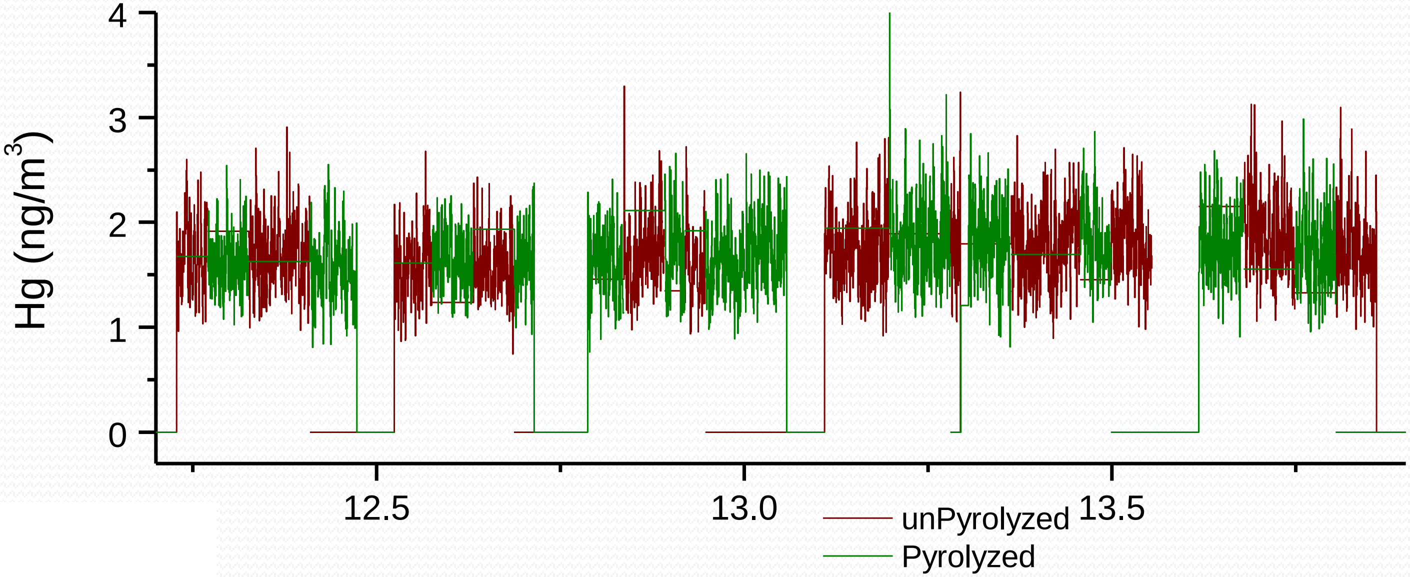
Air Flow - pyrolyzer



- ~15 cm fused Si tubing (3/8” id) partially filled with Si wool,
- ~ 8 cm wrapped with NiCr wire with constant voltage applied
- Continuous air flow through both pathways

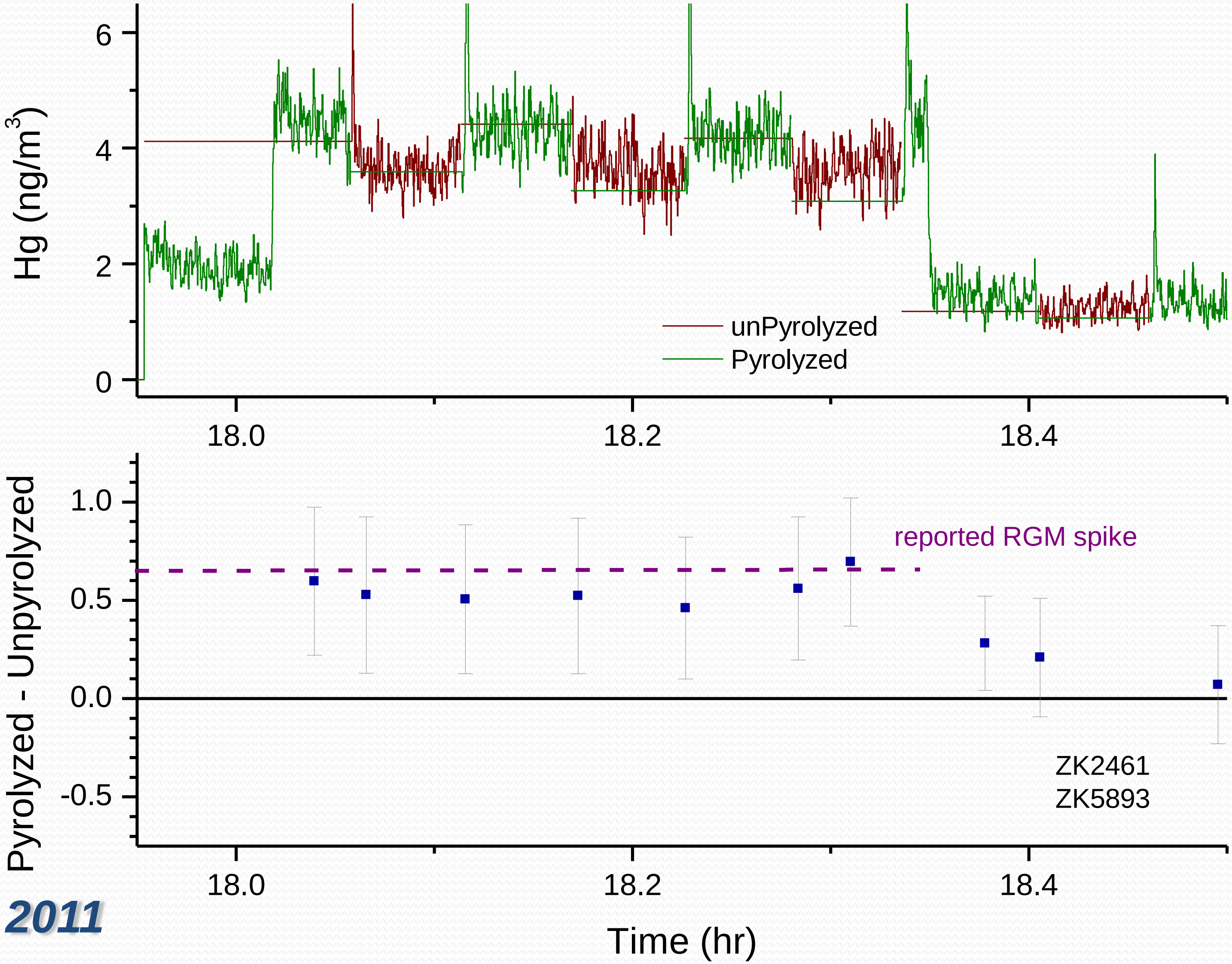


TGM Detection



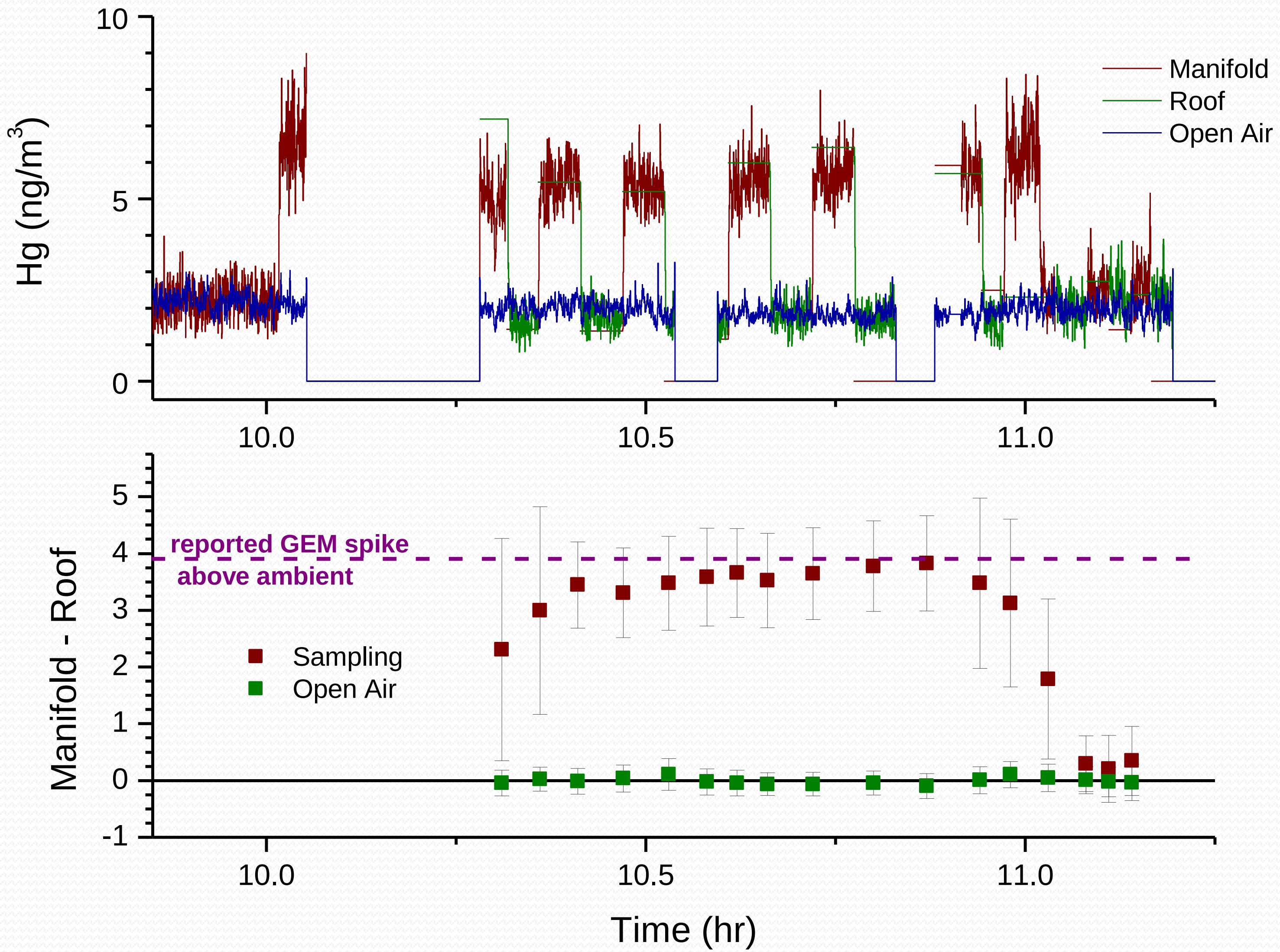
Sept 14, 2011

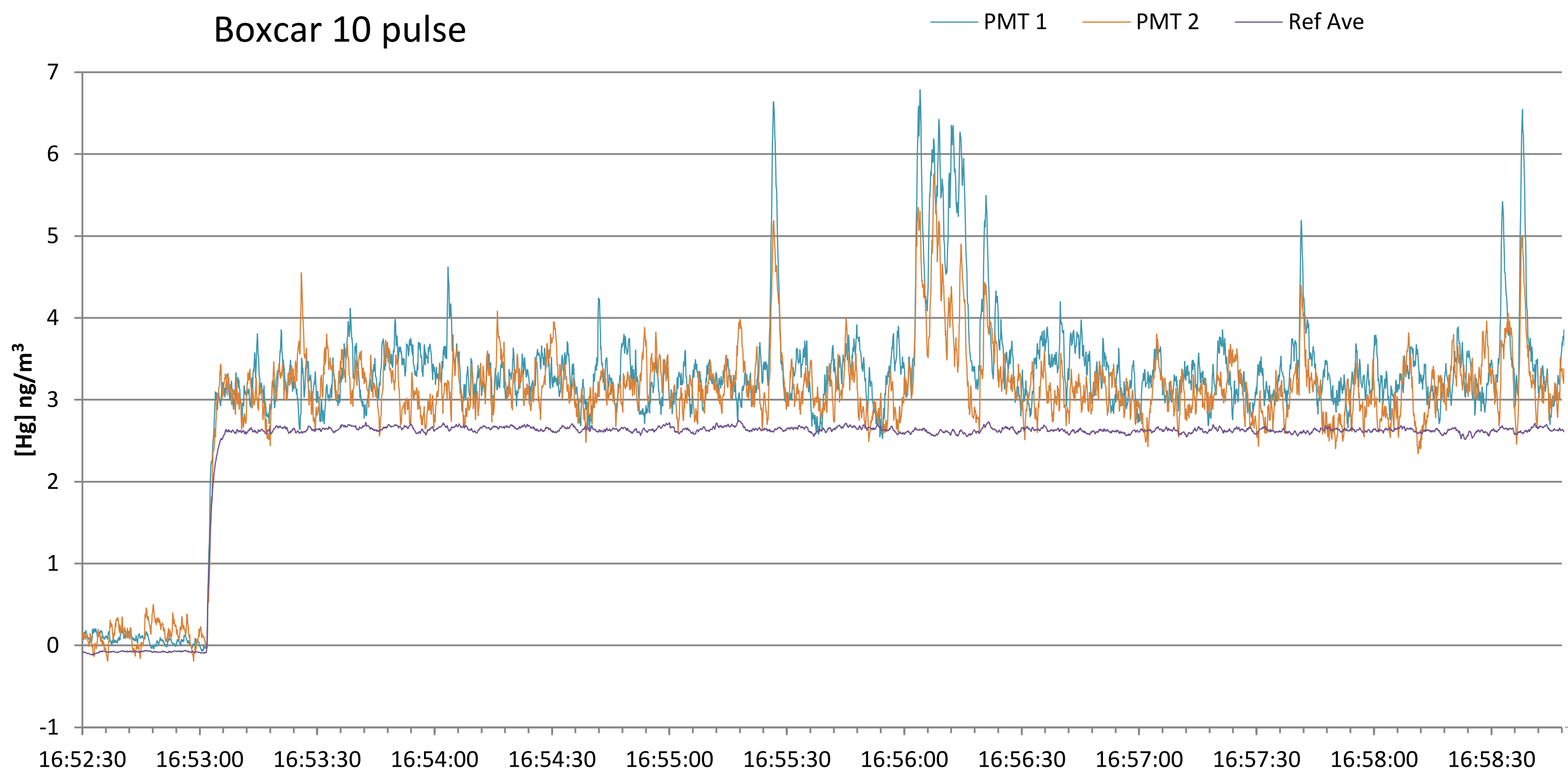
TGM Detection



Sept 14, 2011

Open Air Sampling





Boxcar 10 pulse
PMT 1
PMT 2
Ref Ave
[Hg] ng/m3
7
6
5
4
3
2
1
0
-1
16:52:30
16:53:00
16:53:30
16:54:00
16:54:30
16:55:00
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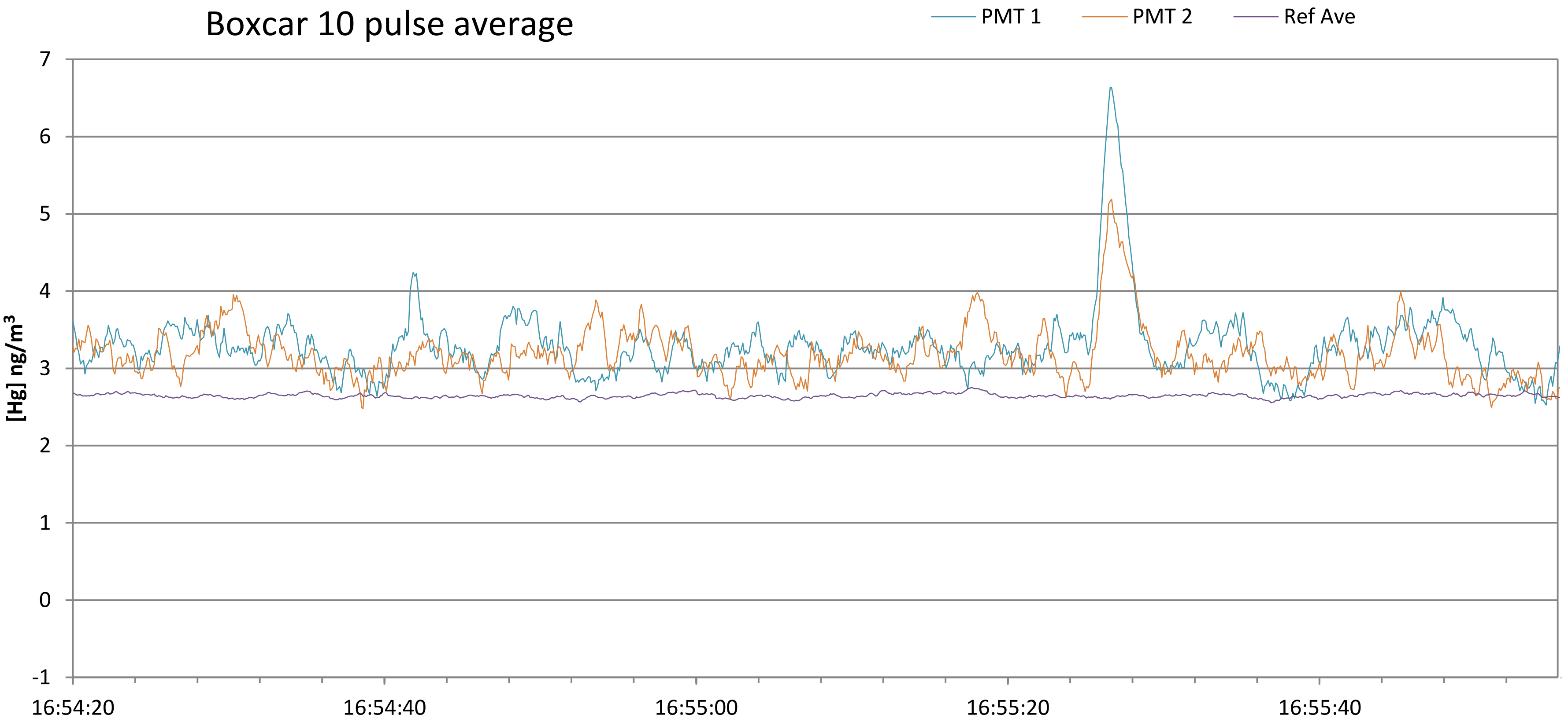
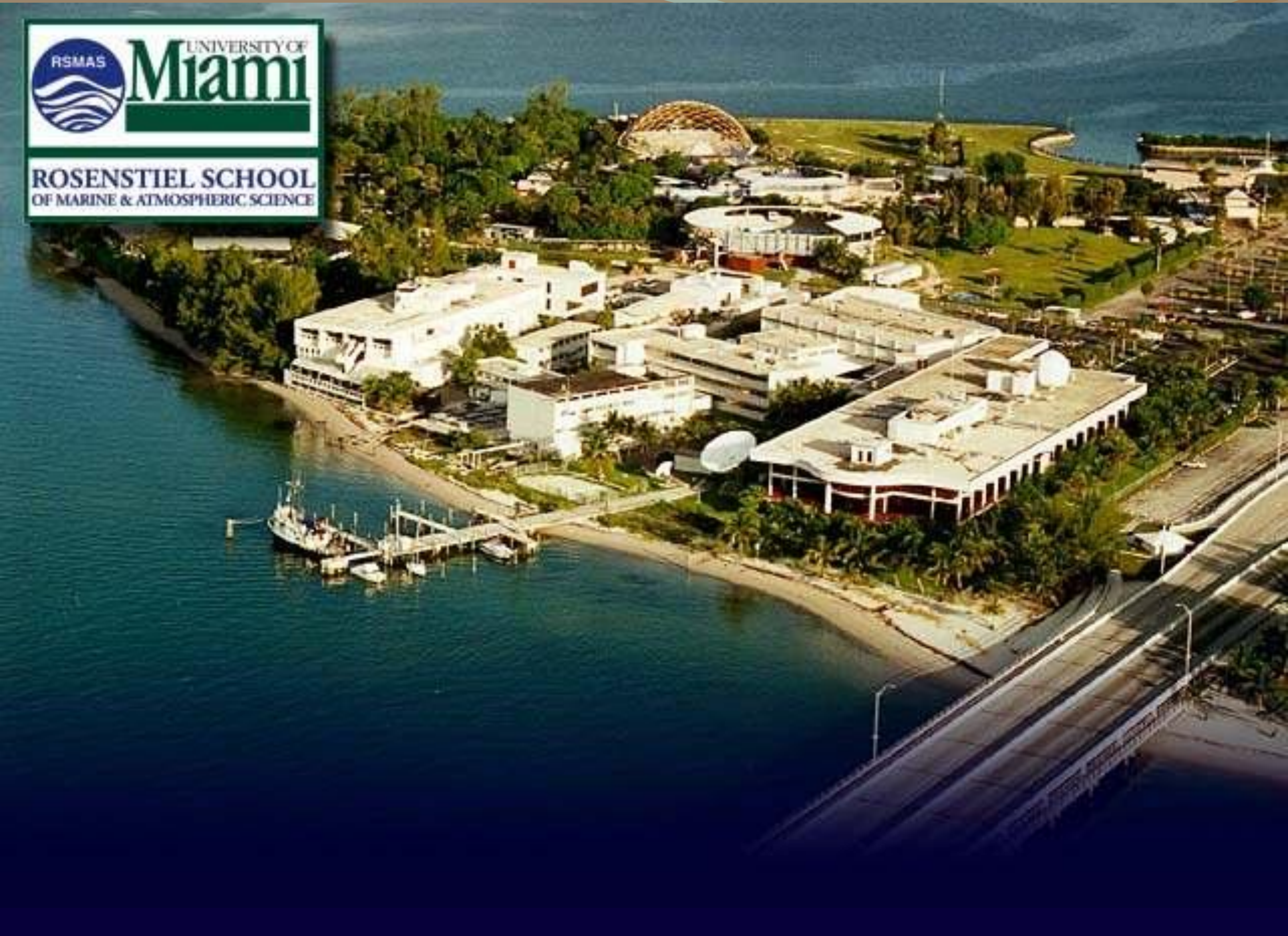
16:56:00
16:56:30
16:57:00
16:57:30
16:58:00
16:58:30



Boxcar 10 pulse average
PMT 1
PMT 2
Ref Ave
[Hg] ng/m3
7
6
5
4
3
2
1
0
-1
16:54:20
16:54:40
16:55:00
16:55:20
16:55:40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OF MARINE & ATMOSPHERIC SCIENCE