QCLS calibrations and sample conditioning of in-situ CO_2, CH_4, N_2O, CO measurements by absorption spectroscopy

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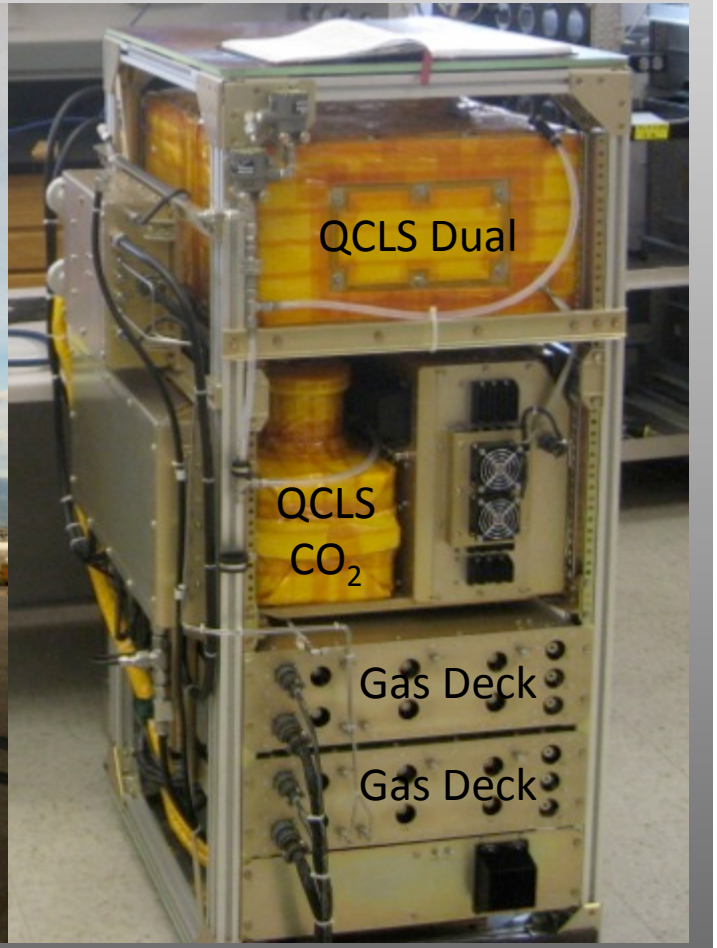
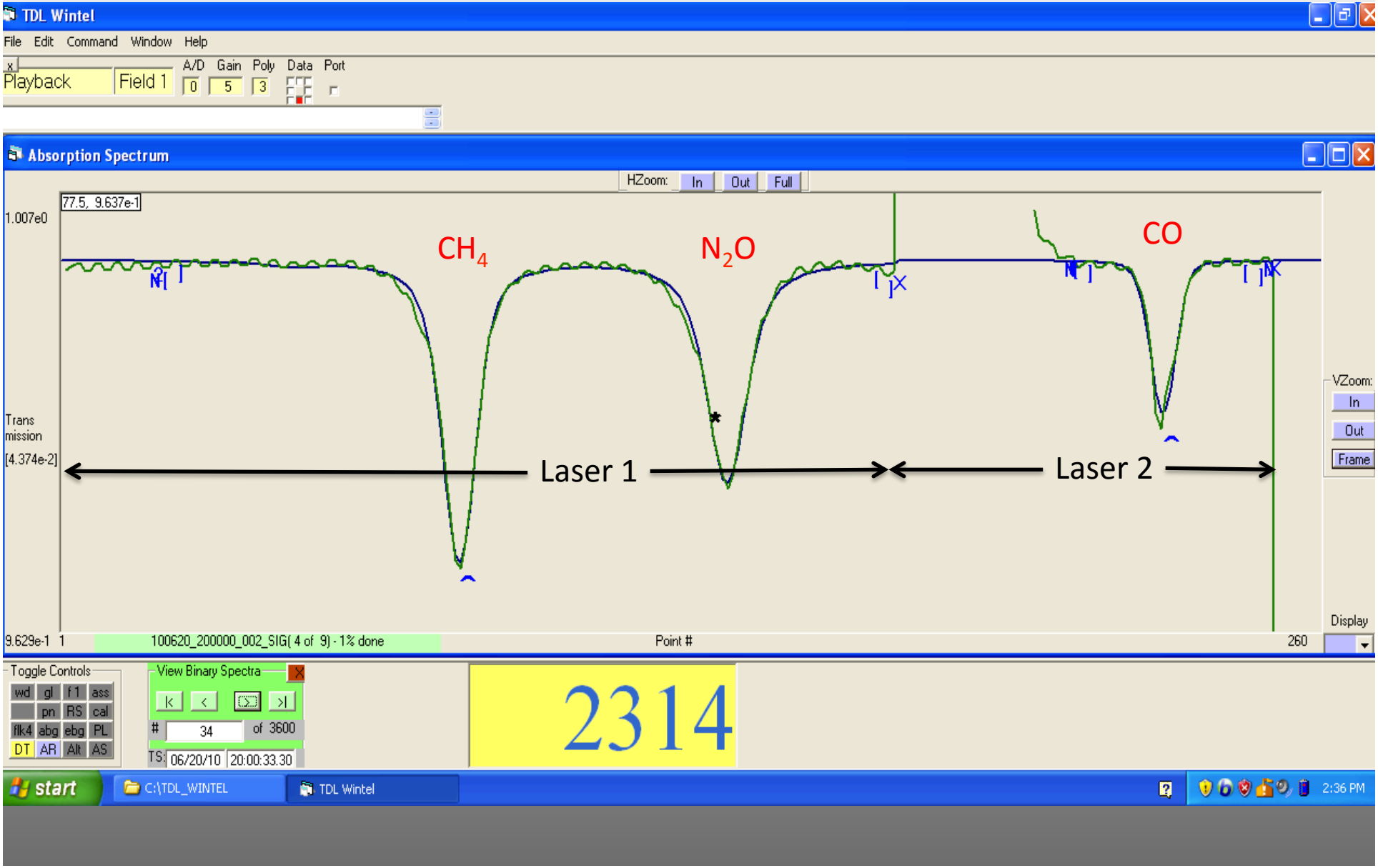


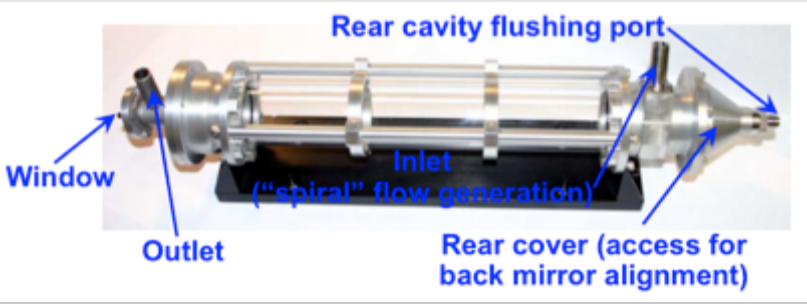
QCLS DUAL

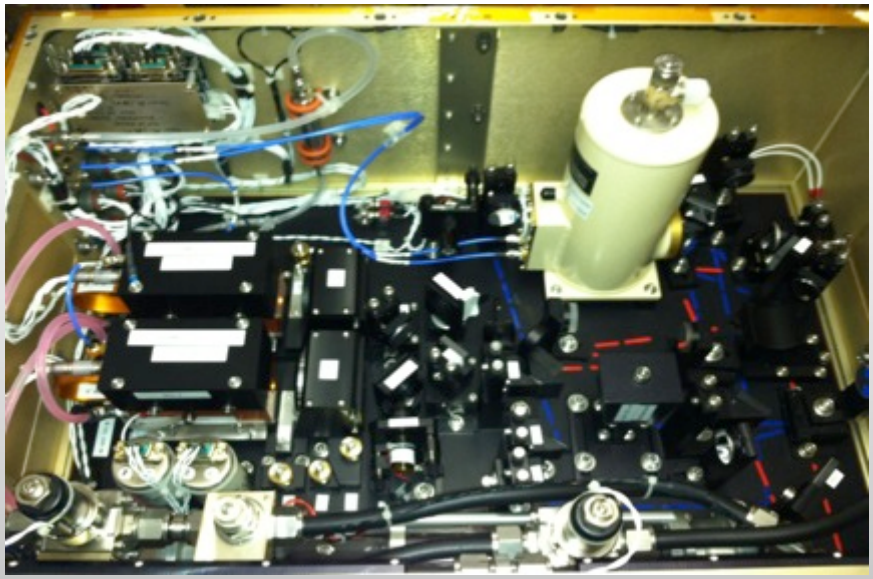
QCLS: Dual TDL Wintel Screenshot

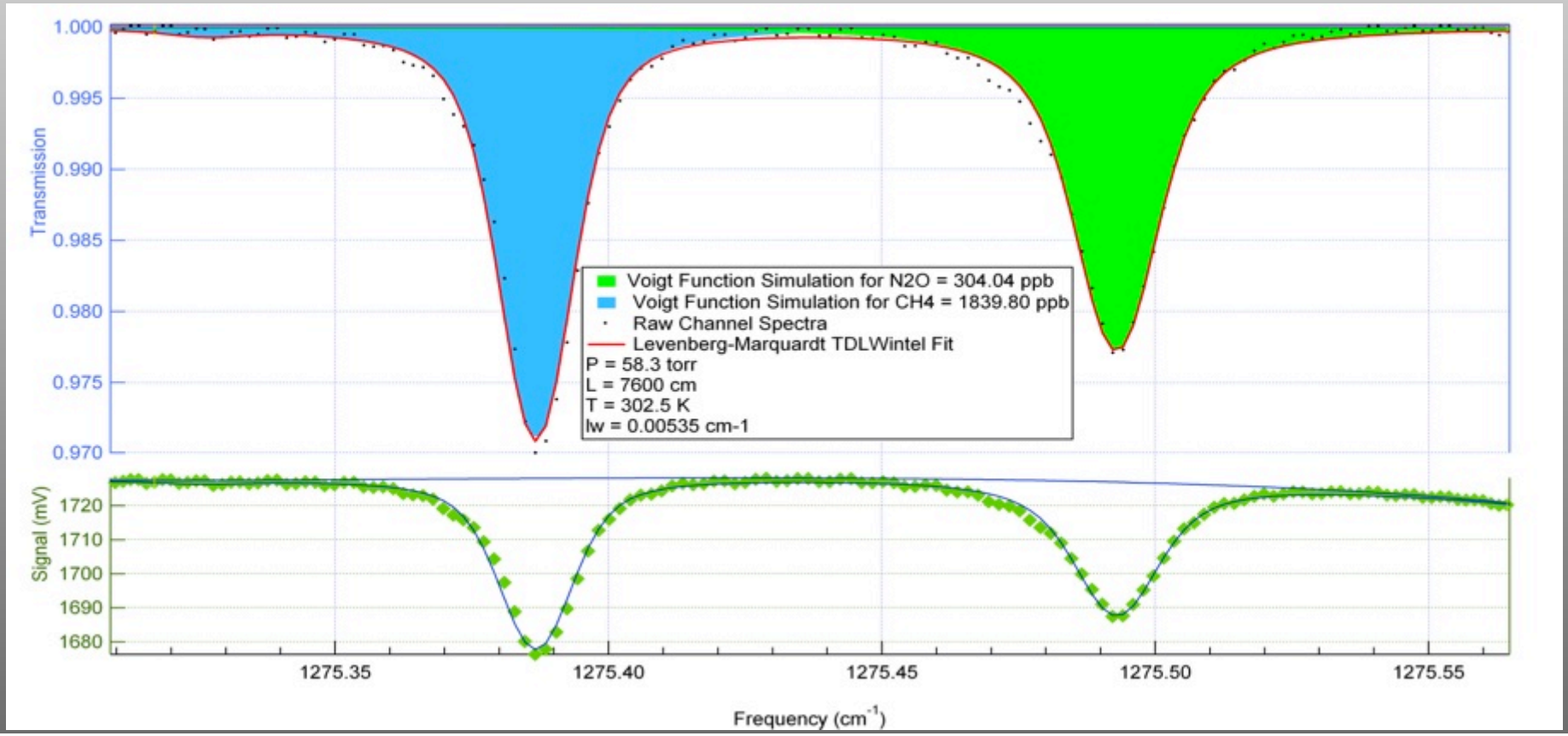


QCLS: Dual Laser 1

CH_4: 1σ = 0.5 ppb & N_2O: 1σ = 0.09 ppb

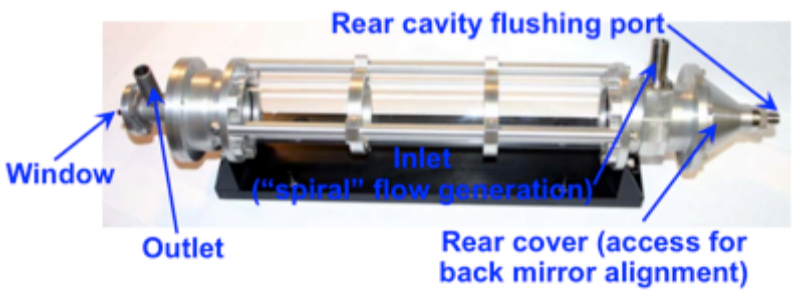


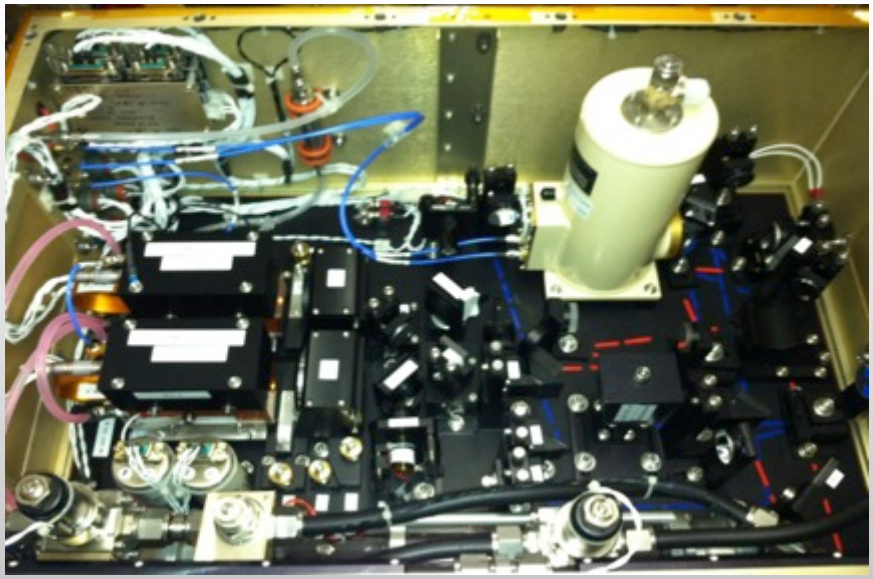


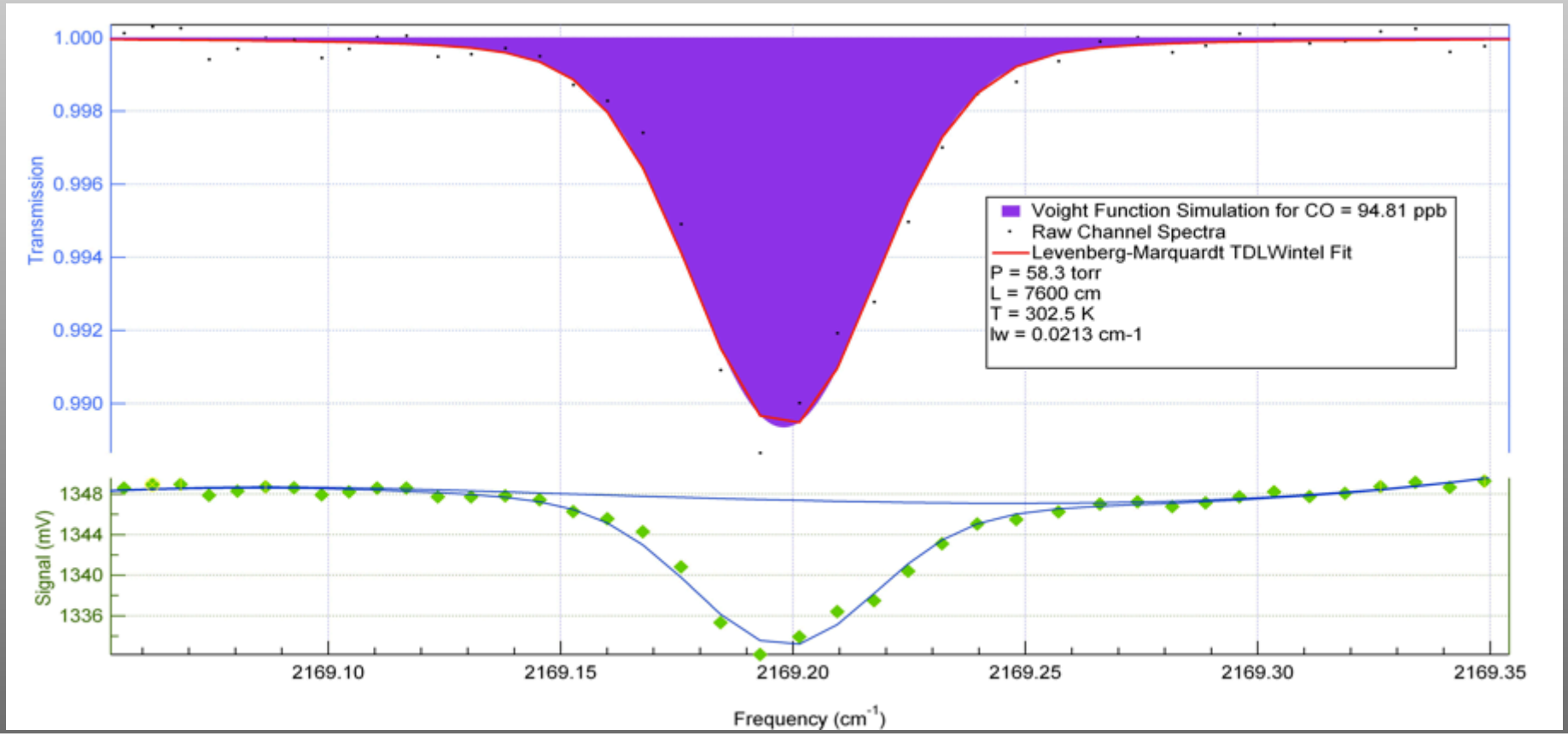


QCLS: Dual Laser 2

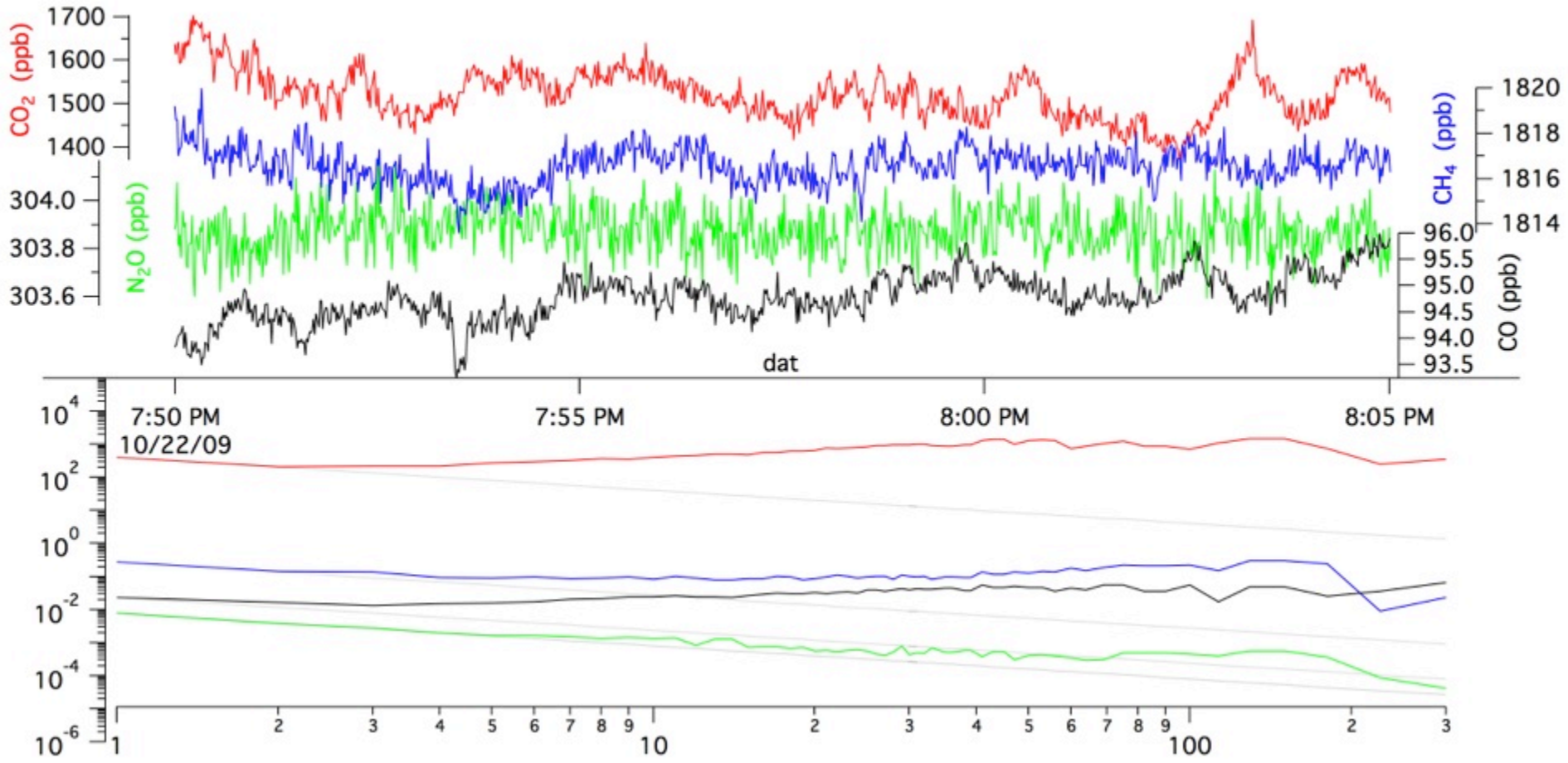
CO: 1σ = 0.15 ppb







QCLS: Allan Variance (in-flight)



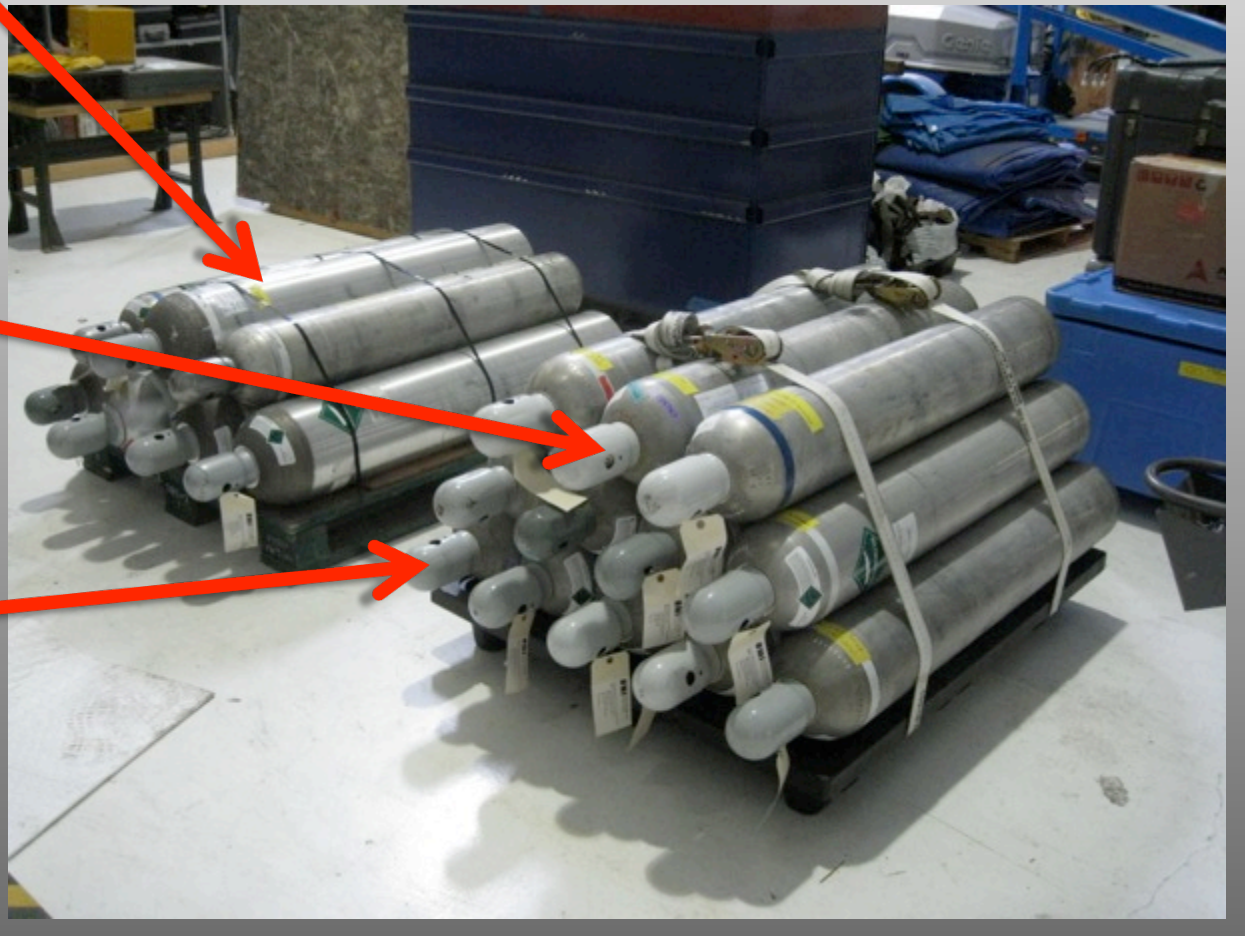
AVAR	CO_2	CH_4	N_2O	CO
1-sec	20	0.5	0.09	0.15
10-sec	20	0.28	0.04	0.15
300-sec			0.007	

QCLS Dual: Calibration Cylinders

"Primaries":
5 cylinders (50 L) calibrated by NOAA with varying CH_4,N_2O, CO content spanning range of "Secondaries"

"Secondaries":
Cylinders (size AL) calibrated using the QCLS Dual instrument and "primaries" and used to fill GasDecks

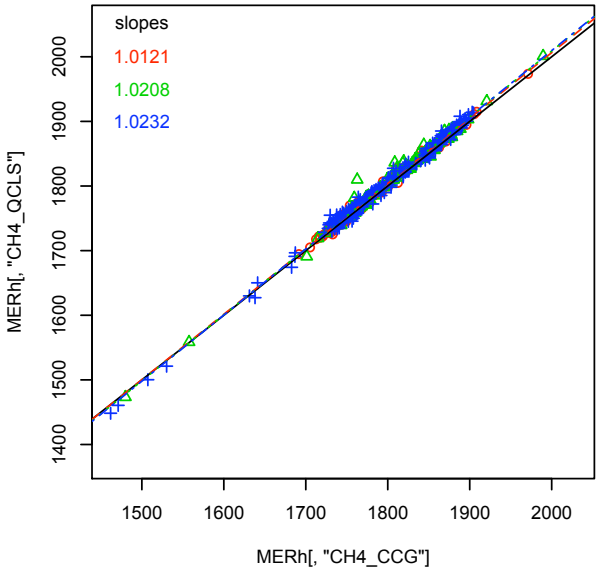
"Zeros":
Cylinders with ultra-zero air used for various purposes

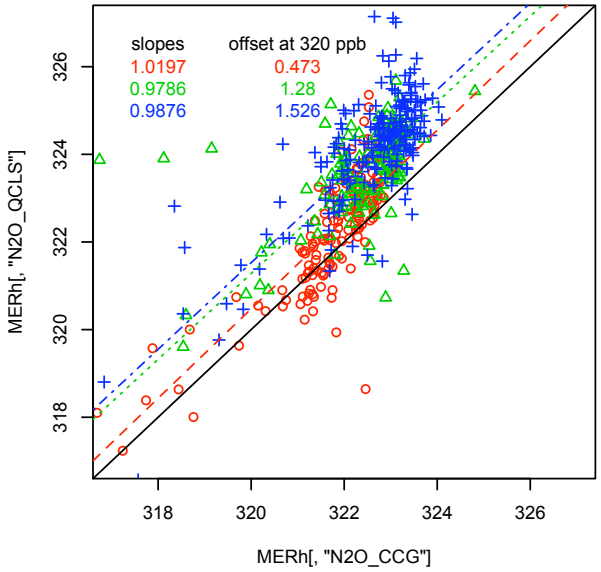


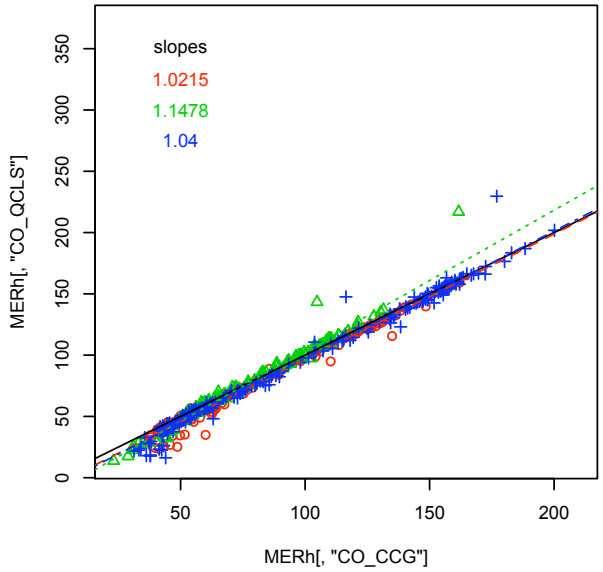
QCLS Dual: Primary Values (B. Hall)

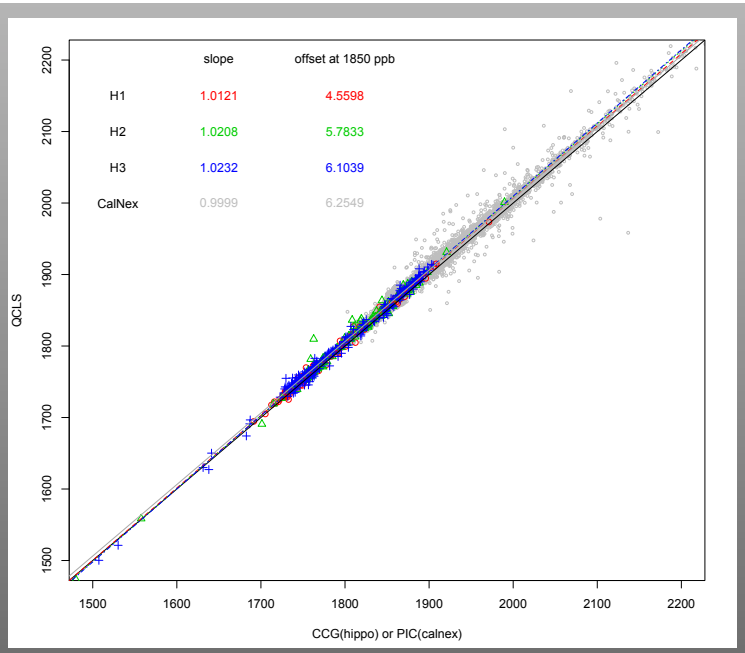
Tag	Tank ID	Date	N_2O	SD	CH_4	SD	CO	SD
Primary 5	ND29403	8/30/2007	248.12	0.10	490.5	2.4	21.5	0.1
Primary 5	ND29403	6/21/2011	247.85	0.11	486.8	0.2	22.7	0.4
			0.27		3.7		-1.2	
Primary 1	ND24119	7/6/2005	154.6	0.2	991.8	0.3	45.1	0.6
Primary 1	ND24119	6/30/2011	155	0.2	995.2	0.3	50.4	0.2
			-0.4		-3.4		-5.3	
Primary 2	ND24116	7/6/2005	326.92	0.13	1361.2	0.2	102.2	0.4
Primary 2	ND24116	8/16/2011	326.92	0.10	1363.3	0.5	103.5	0.7
			0		-2.1		-1.3	
Primary 3	ND24117	7/11/2005	339.2	0.15	1801.1	0.3	352.6	2
Primary 3	ND24117	6/20/2011	339.43	0.15	1801.1	0.2	352.9	0.5
			-0.23		0		-0.3	
Primary 4	ND24118	5/5/2005	356.39	0.15	2470.9	0.3	980.1	10
Primary 4	ND24118	8/16/2011	357.03	0.16	2466.5	1	982.4	6.7
			-0.64		4.4		-2.3	

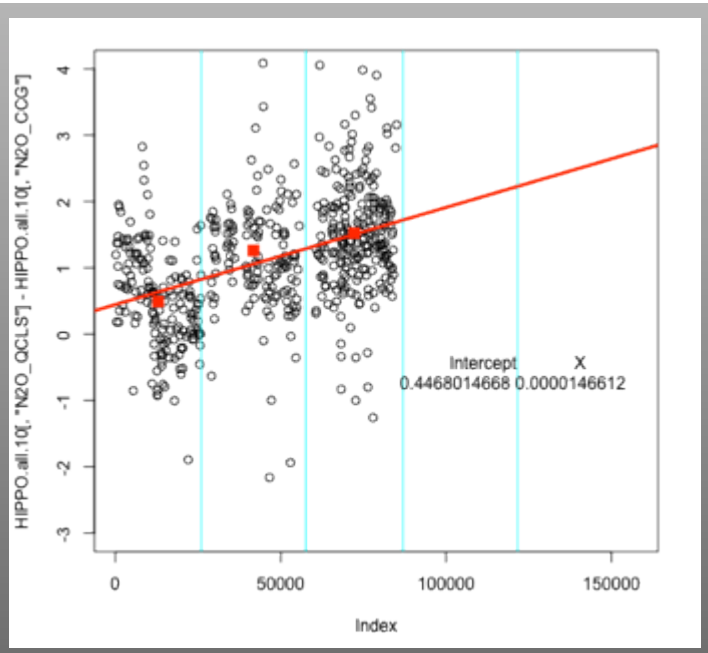
QCLS Dual: Comparisons with CCG



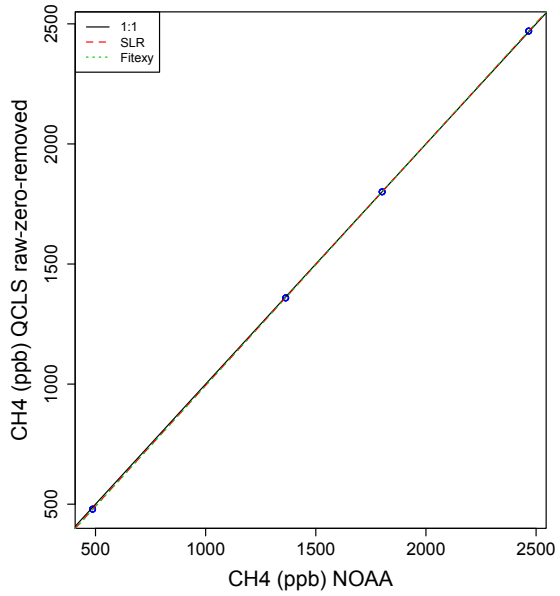


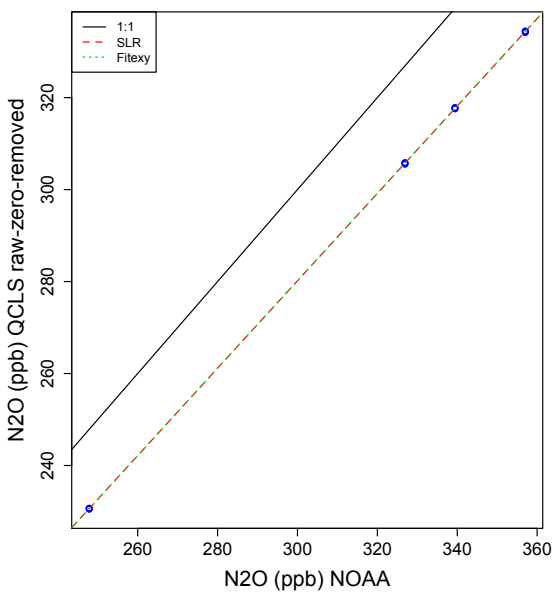


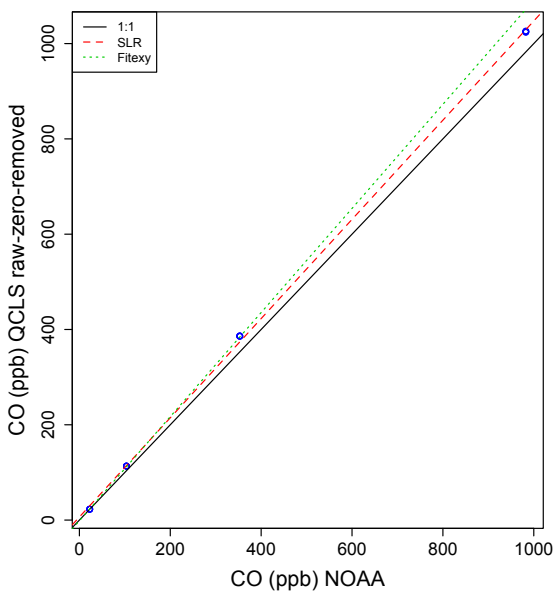


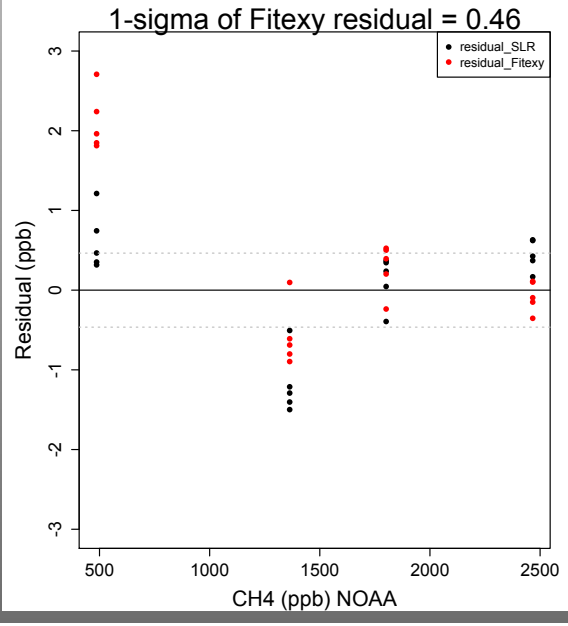


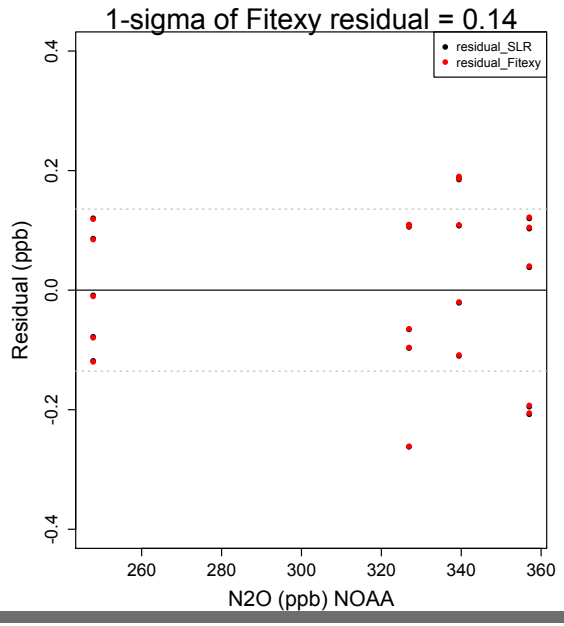
QCLS Dual Linearity

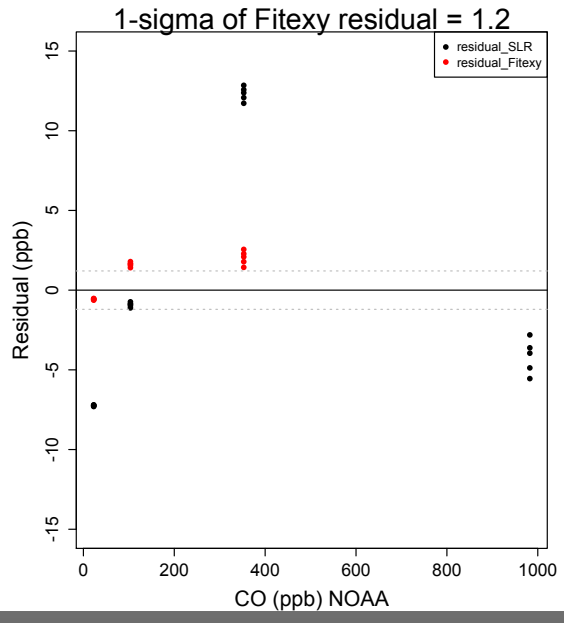




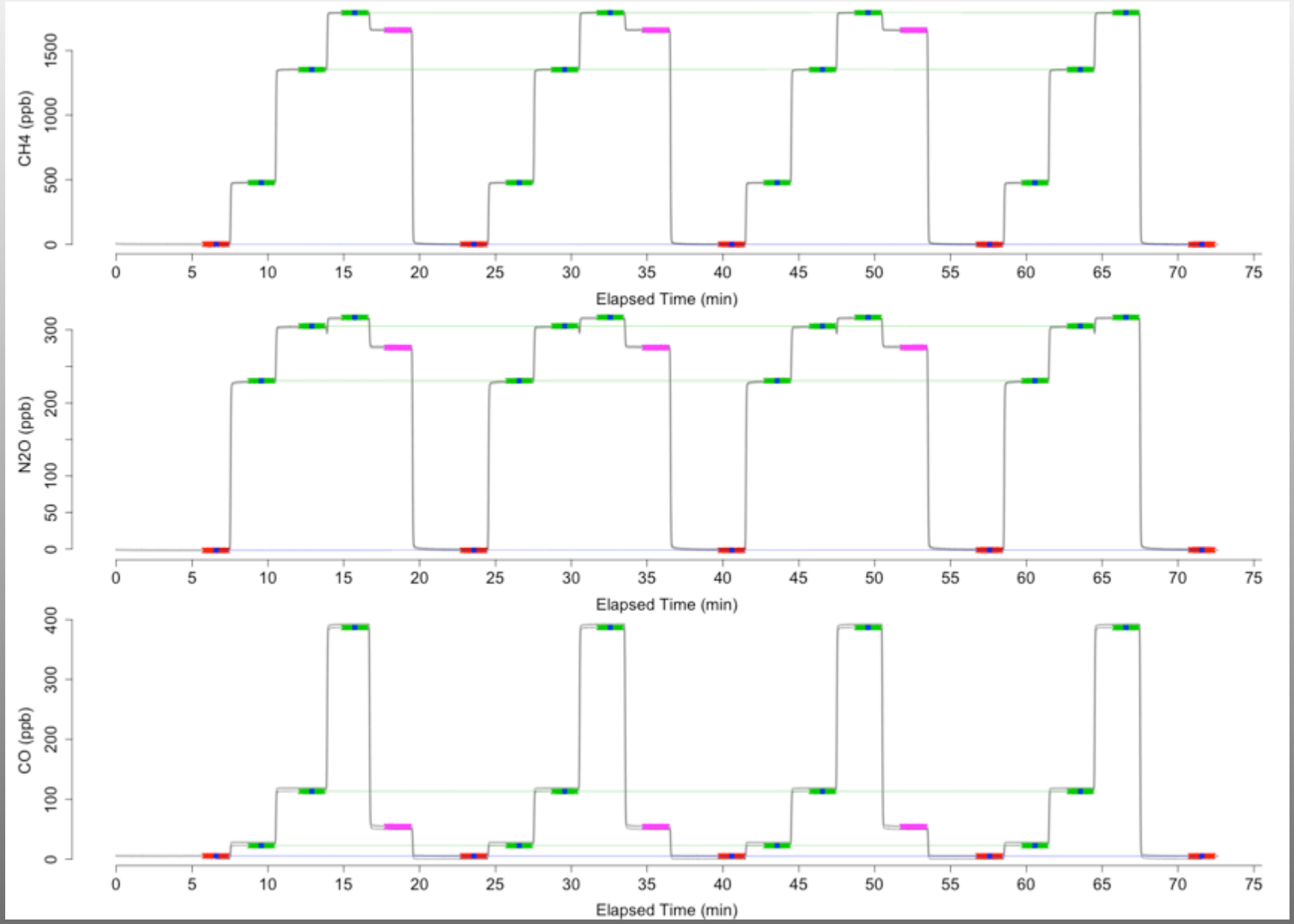




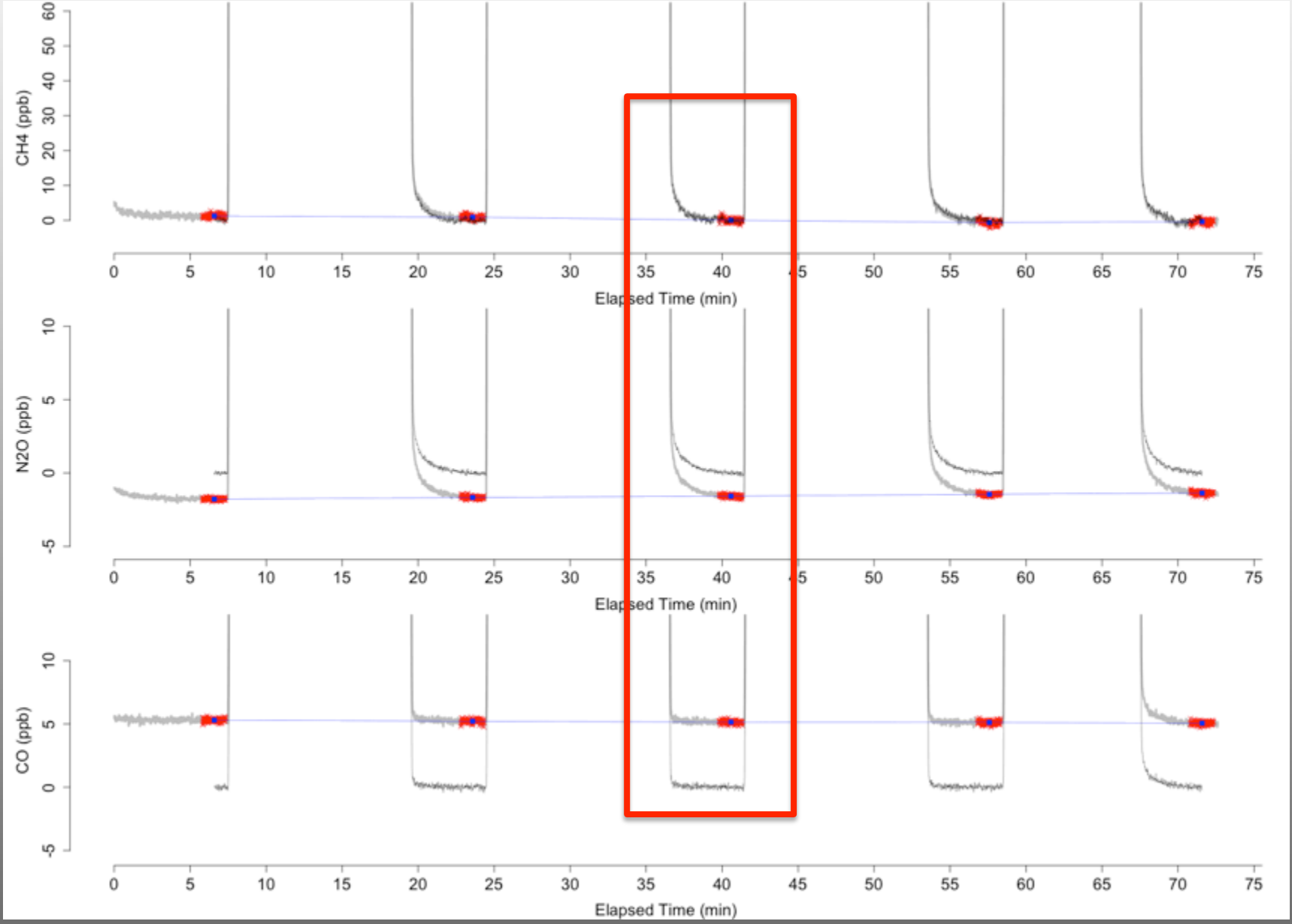




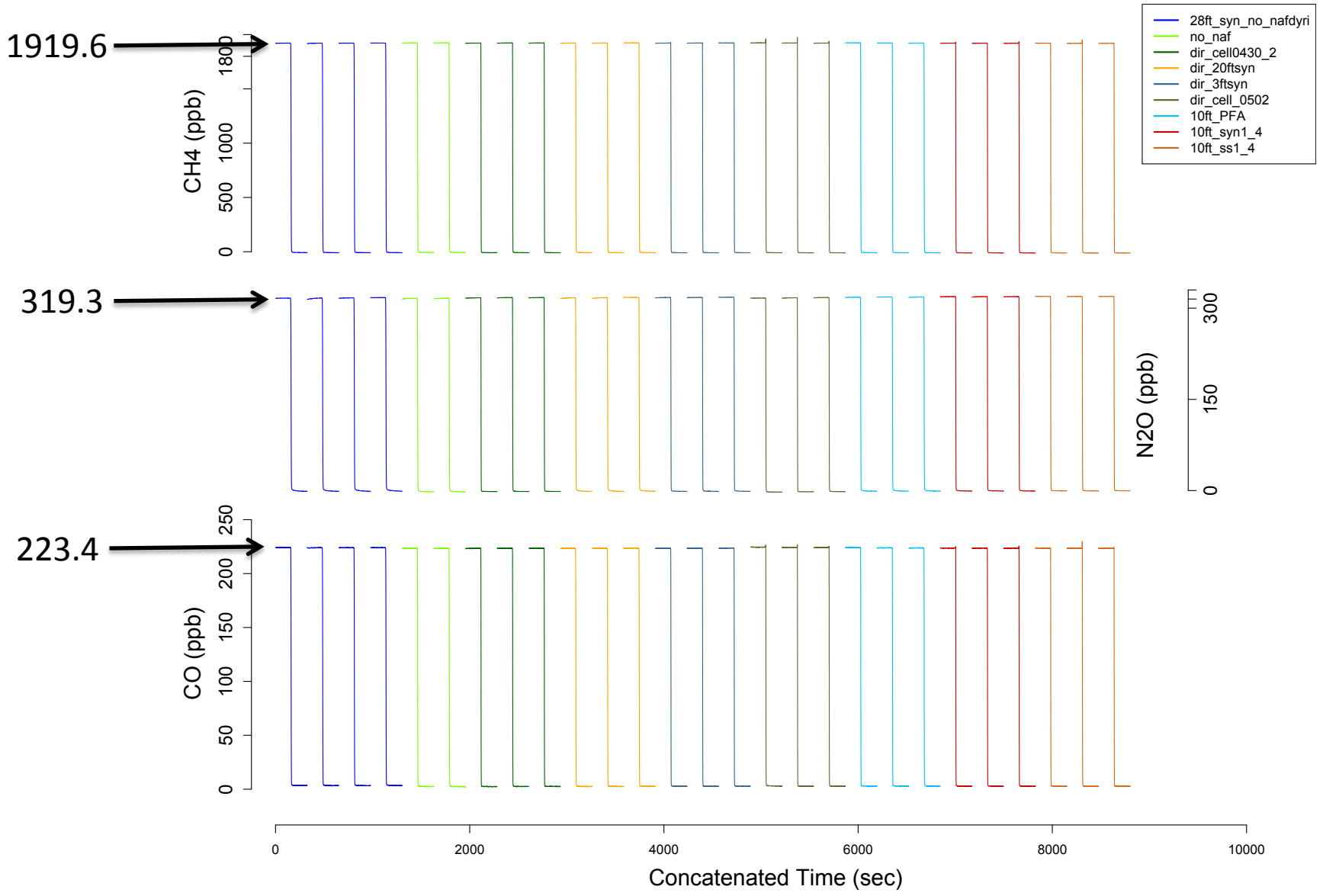
QCLS Secondary Calibrations:



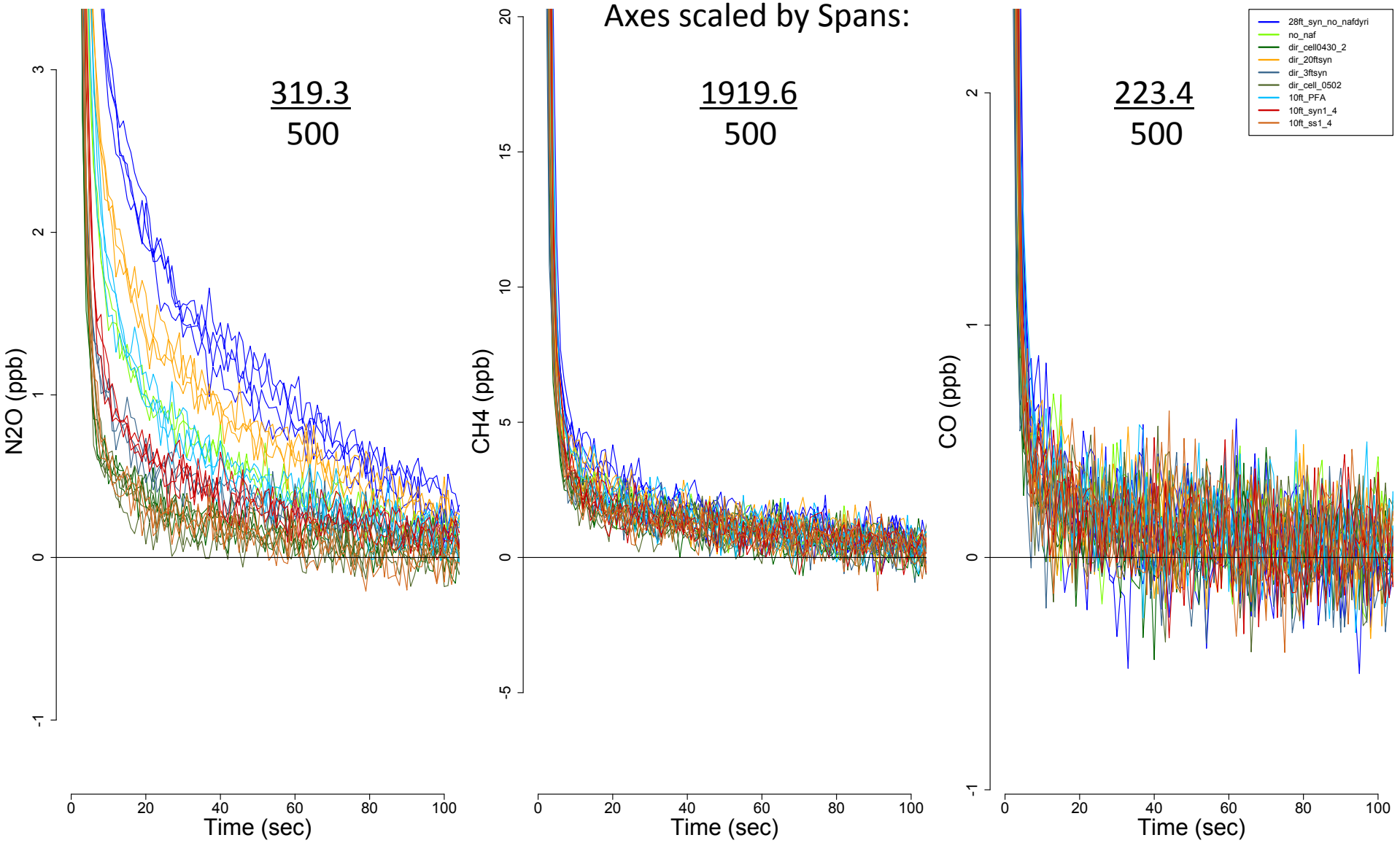
QCLS Secondary Calibrations cont.



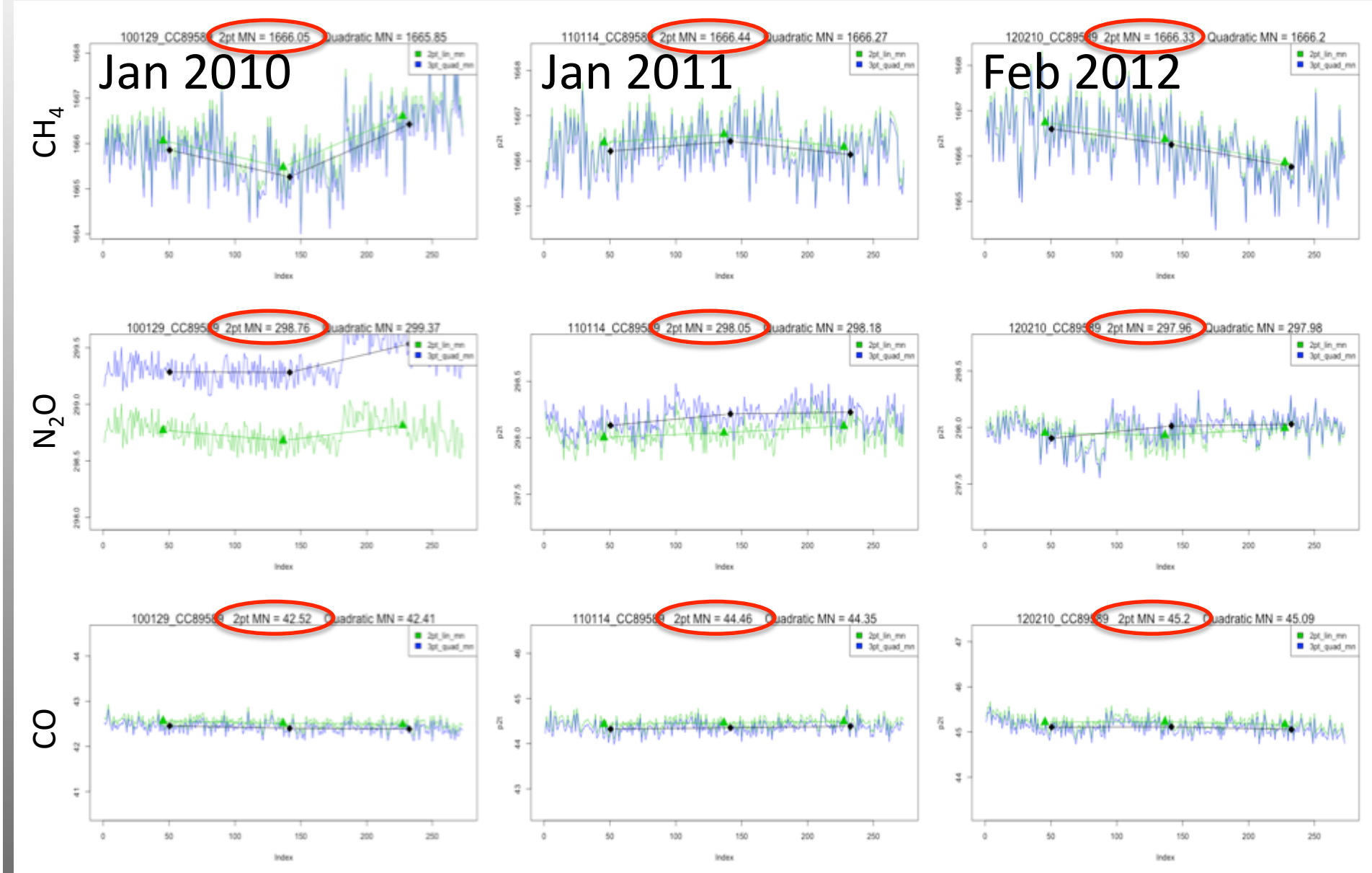
QCLS Dual Equilibration



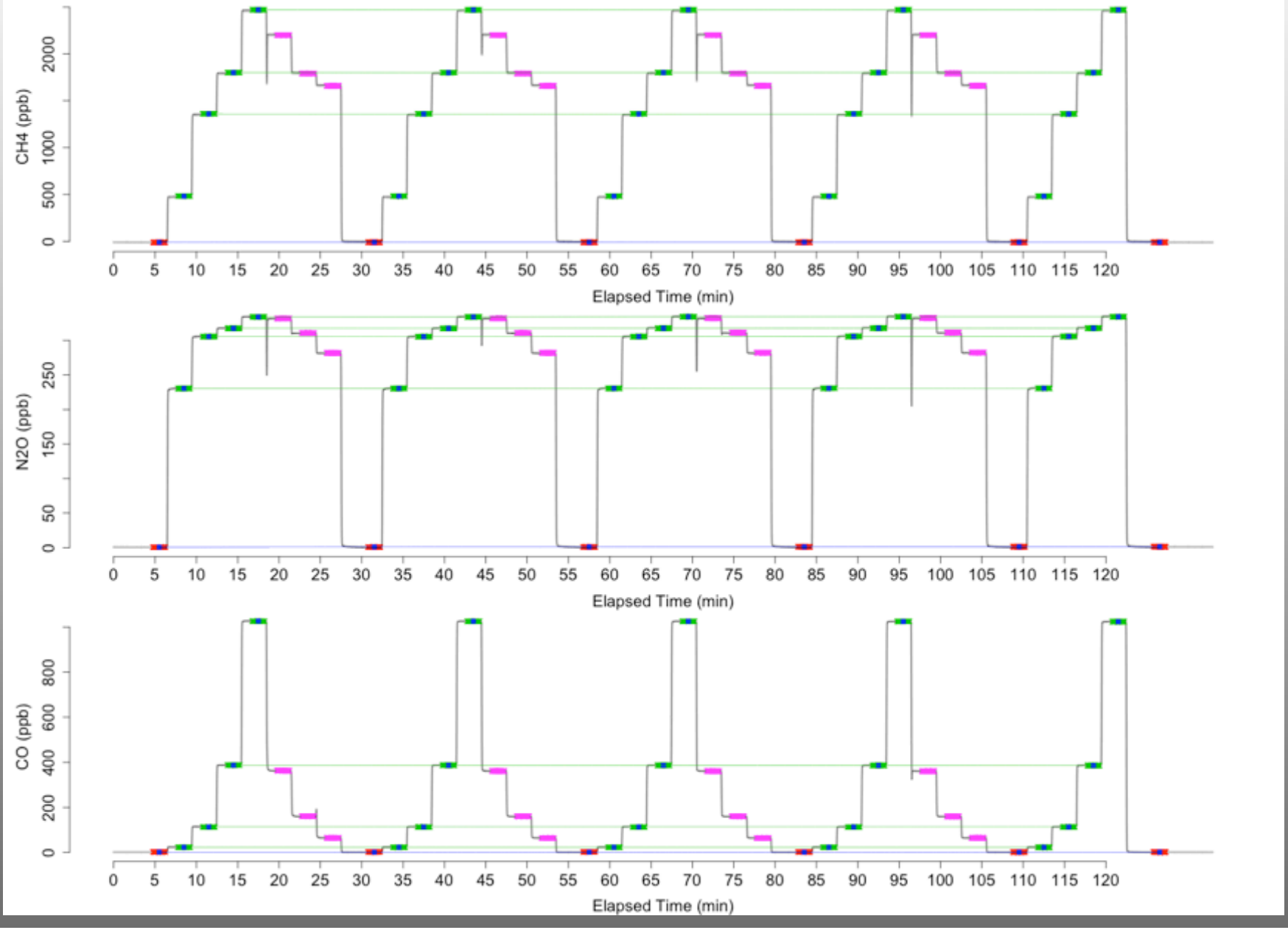
QCLS Dual Equilibration



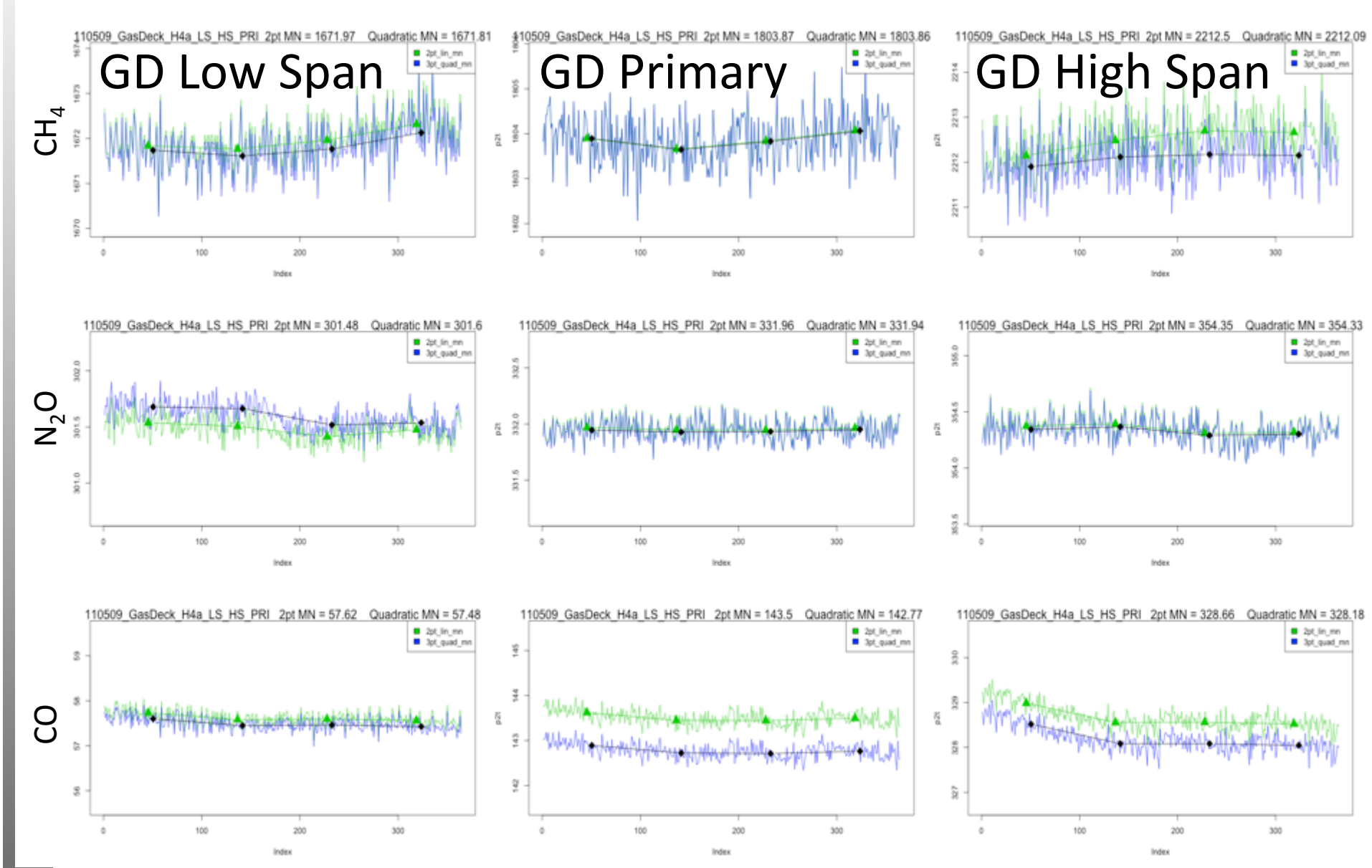
QCLS Secondaries over time



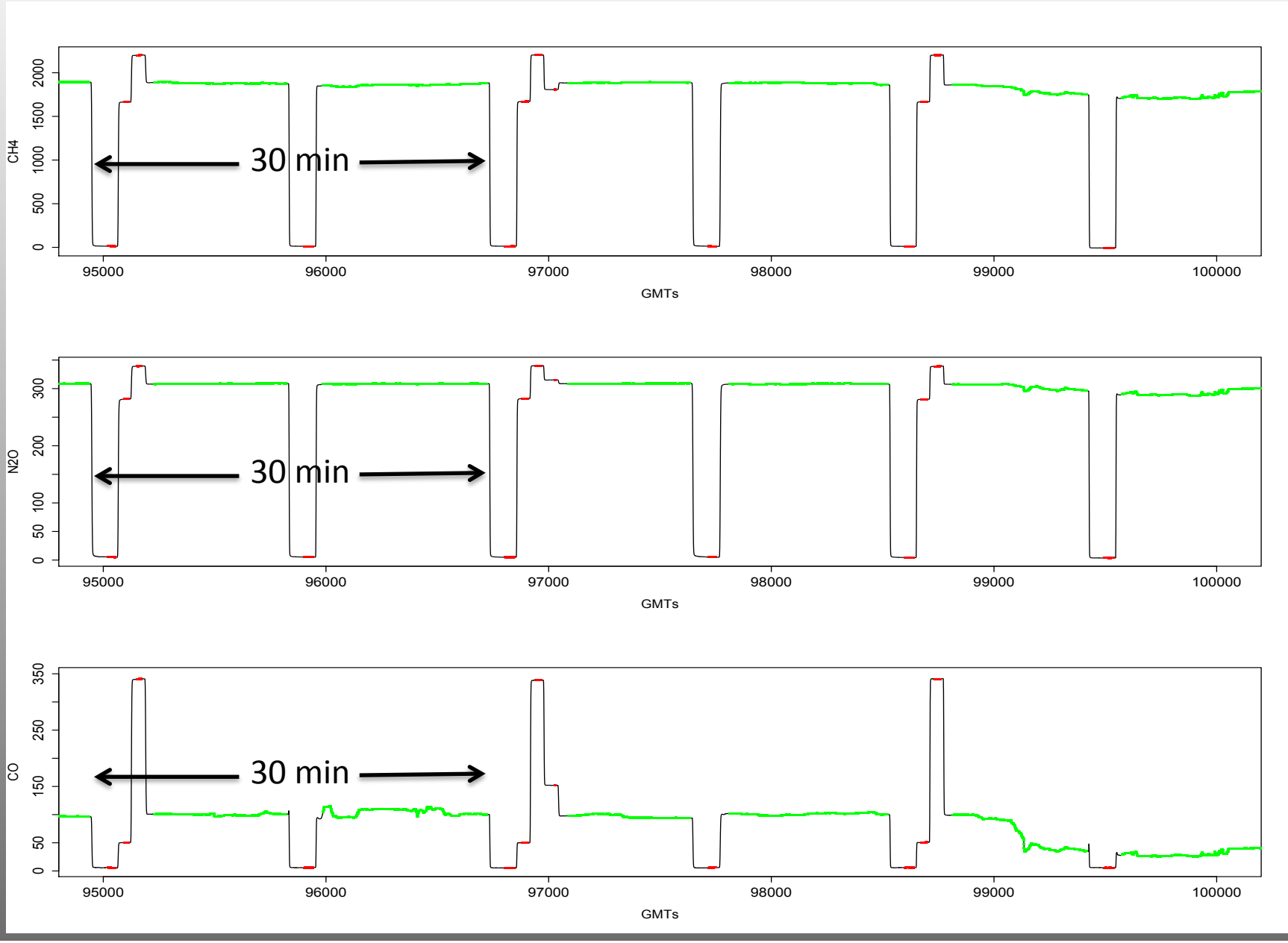
QCLS Gas Deck Calibrations



QCLS Gas Deck Calibrations cont.



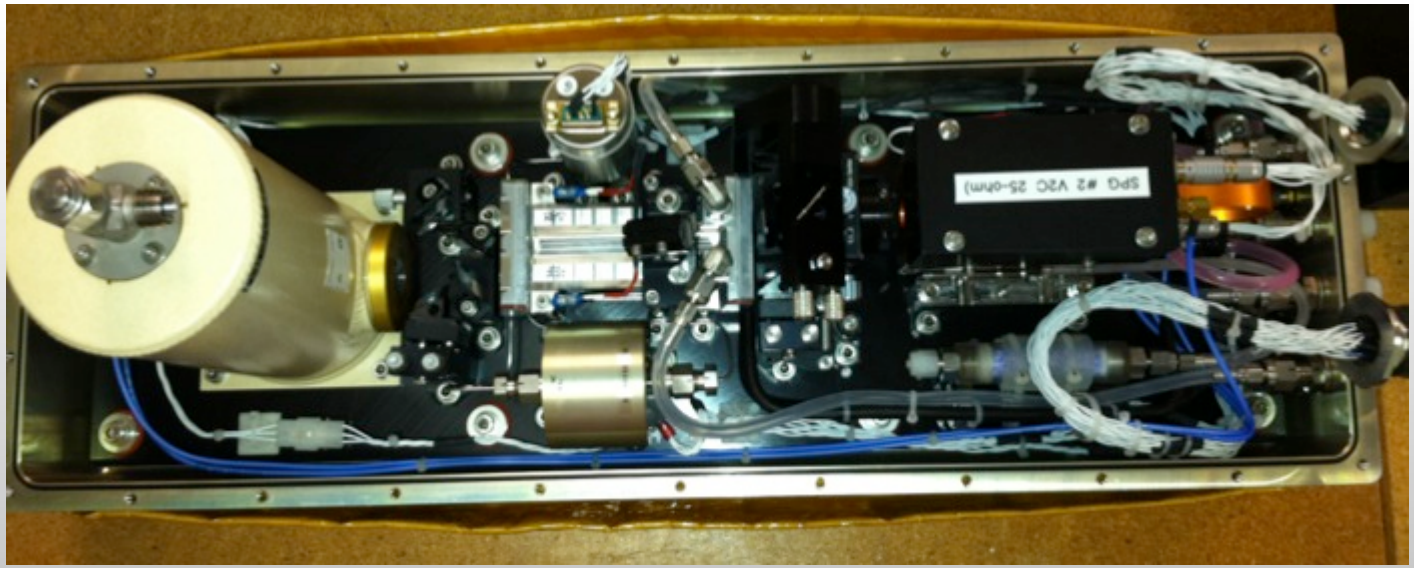
QCLS Dual: In flight calibrations

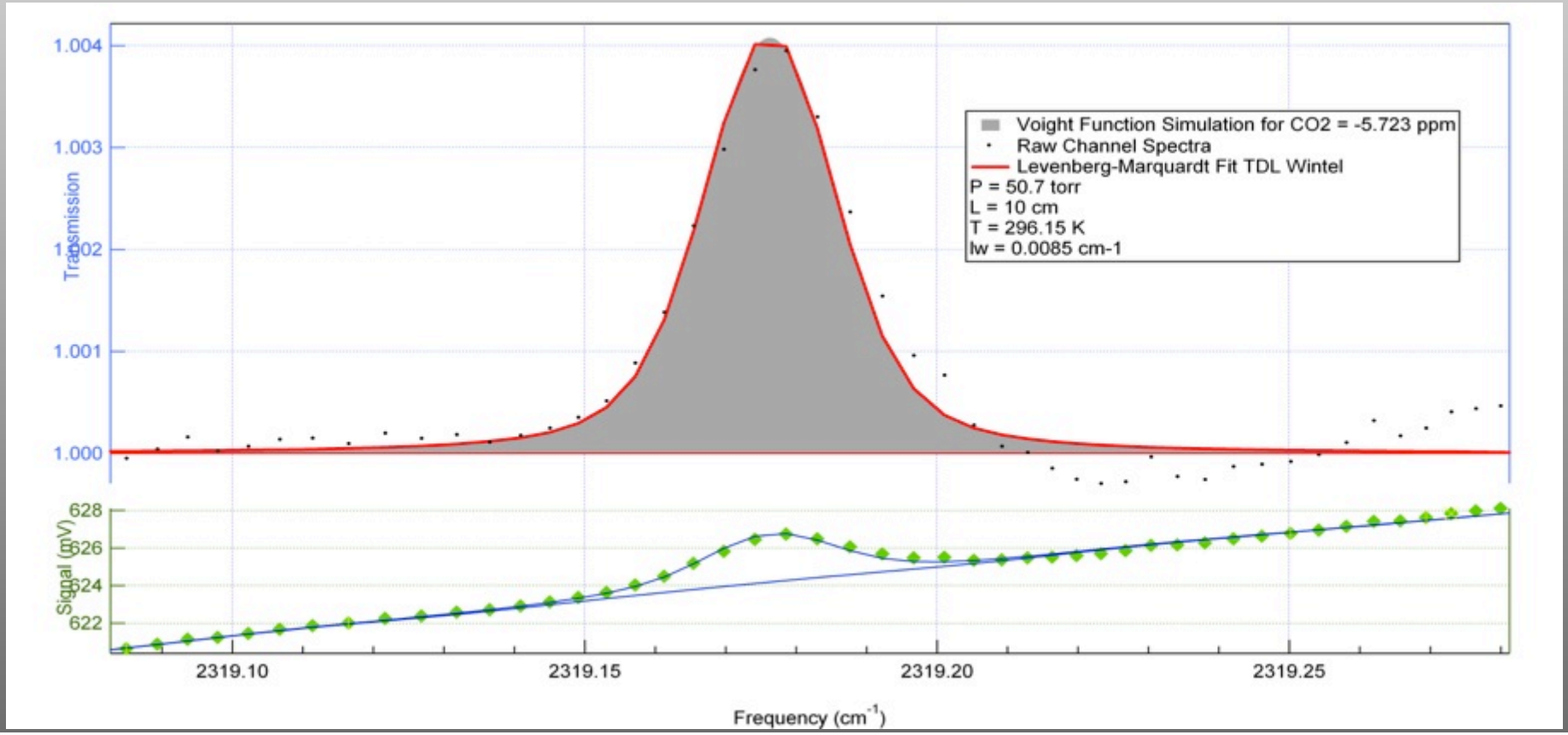


QCLS CO_2

QCLS: CO_2

CO_2: 1σ = 20. ppb





QCLS CO_2: Calibration Cylinders

Different Set of Primaries used to calibrate Secondaries

- CO_2 Gas Deck also calibrated using Primaries but values of secondary fill tanks used for in-flight cals (with a few caveats)

- Isotopic Issue – ground cal unit is a Licor NDIR whereas QCLS CO2 scans (differentially) a $^{12}C^{16}O^{16}O$ absorption line

- The isotopic issue is on the order of 0.1 ppm depending on the concentration and isotopic composition of the secondaries used in the QCLS CO_2 gas deck

QCLS CO_2: Isotopic Corrections

The GSE/OMS/ER2 Instruments are all Licor model 6251.
Tohjima eta l. (2009) characterized the sensitivity of 3 Licors (two 6252 and one 6262) to each of the isotopologues of CO_2 that can affect retrieved CO_2 measurements.
They use a Relative Molar Response (RMR) value for each isotopologue to calculate the effective change in concentration determined for each isotopologue (See their Table 4).

We can roughly define the isotopic composition of the atmosphere as $\delta^{13}C$ = -10 ‰ and $\delta^{18}O$ = 40 ‰ according to:

$$\delta^{13}C_{CO_2} = \left[\frac{R13_{sam}}{R13_{vpdb}} - 1\right] \cdot 1000$$

$$\delta^{18}O_{CO_2} = \left[\frac{R18_{sam}}{R18_{vsmow}} - 1\right] \cdot 1000$$

And in order to account for the RMR we need to subtract ~0.059 ppm* from the GSE side of the calibration of secondaries, then add 0~.16 ppm* for the QCLS side of the measurement to get the sampling of the secondaries onto 'atmospheric' isotopic scale so the net effect is ~0.1 ppm offsets.

*functions of concentration, $\delta^{13}C$, and $\delta^{18}O$, and RMR for GSE

QCLS CO_2: akima cal interpolation