

# Update and expansion of the WMO X2004 CH<sub>4</sub> mole fraction scale

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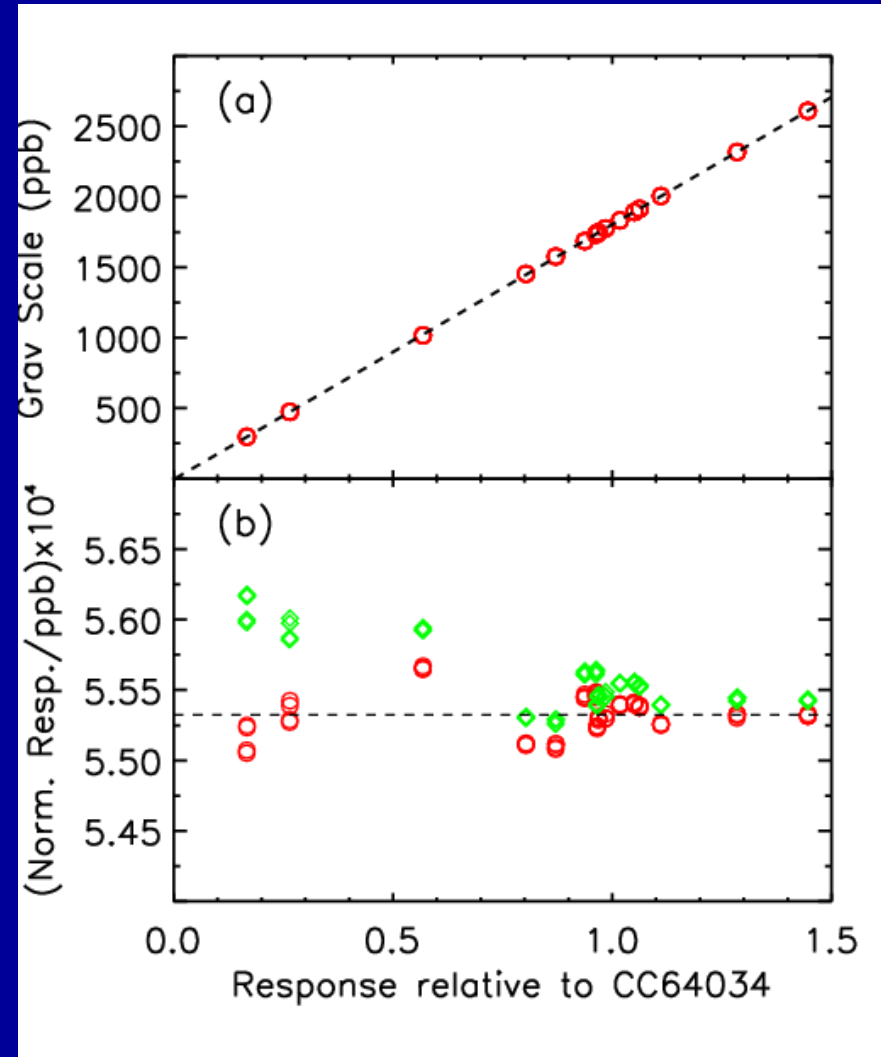
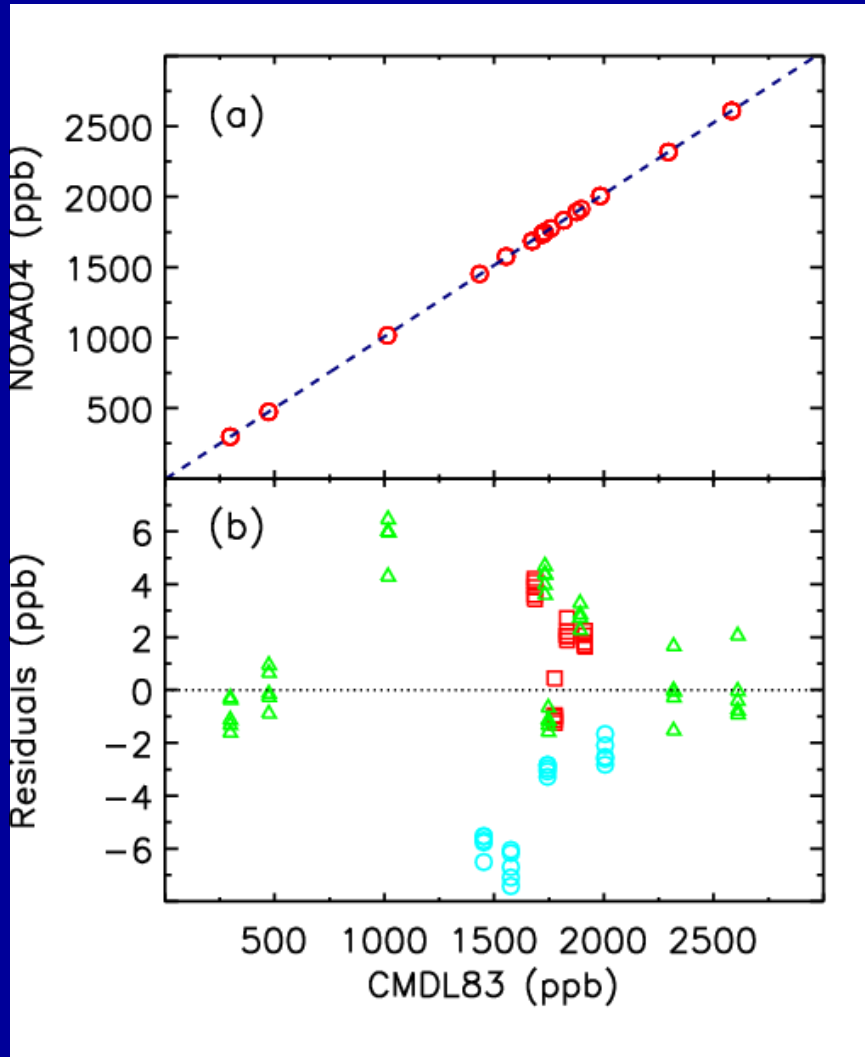
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# Outline

- Reasons for changes
  - Ensure continental measurements are calibrated
  - Account for analytical non-linearity
- New gravimetrically prepared 1° standards
  - 6 standards in range 2200 to 5900 ppb
  - Combined with previous set (300 to 2600 ppb)
- New 2° standards (390 to 5000 ppb)
  - Calibrated with gravimetrically-prepared 1°s
  - Propagate scale with response curve
- How do you update your assigned values?

# X2004 CH<sub>4</sub> Primary Standards

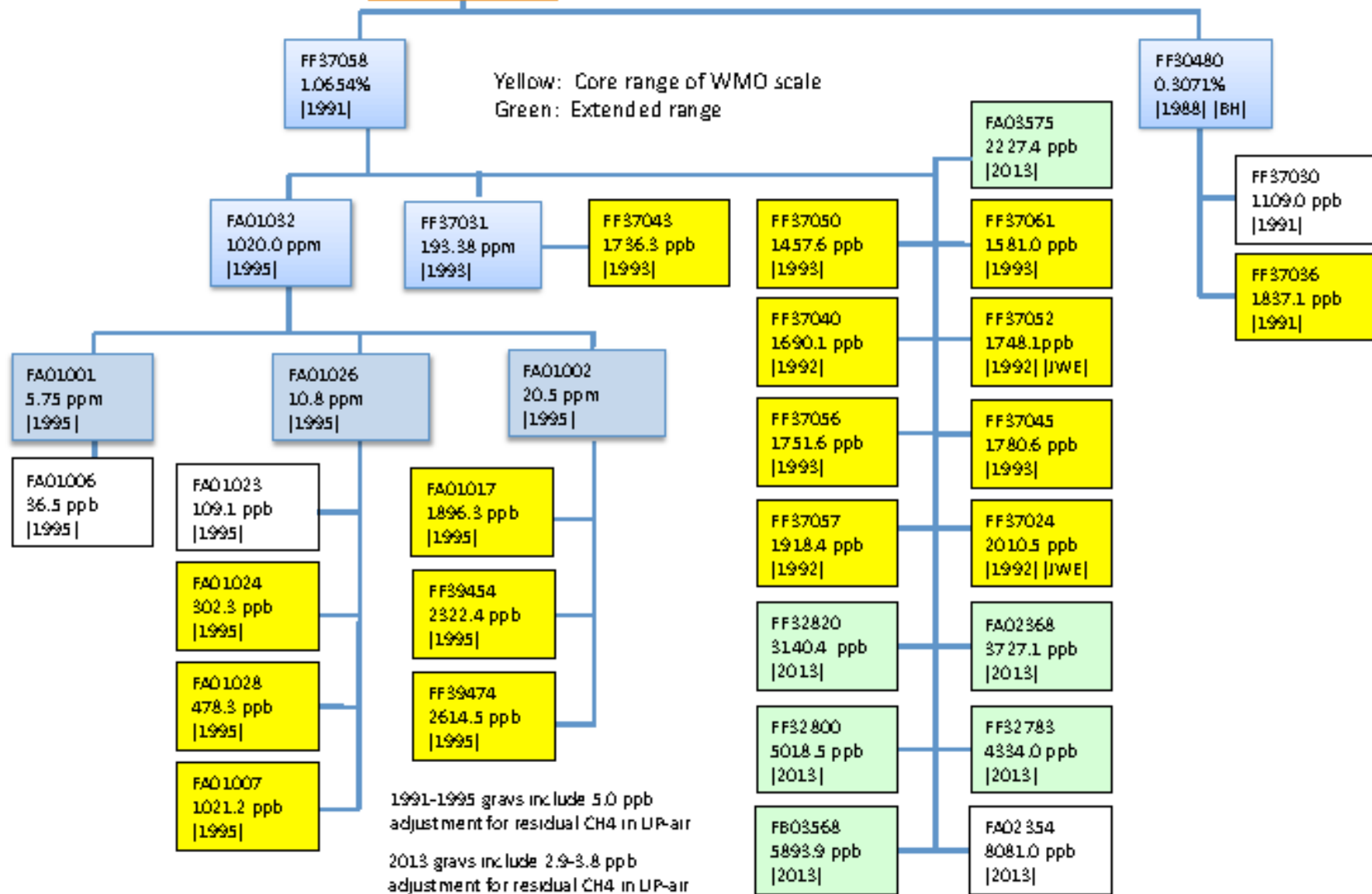


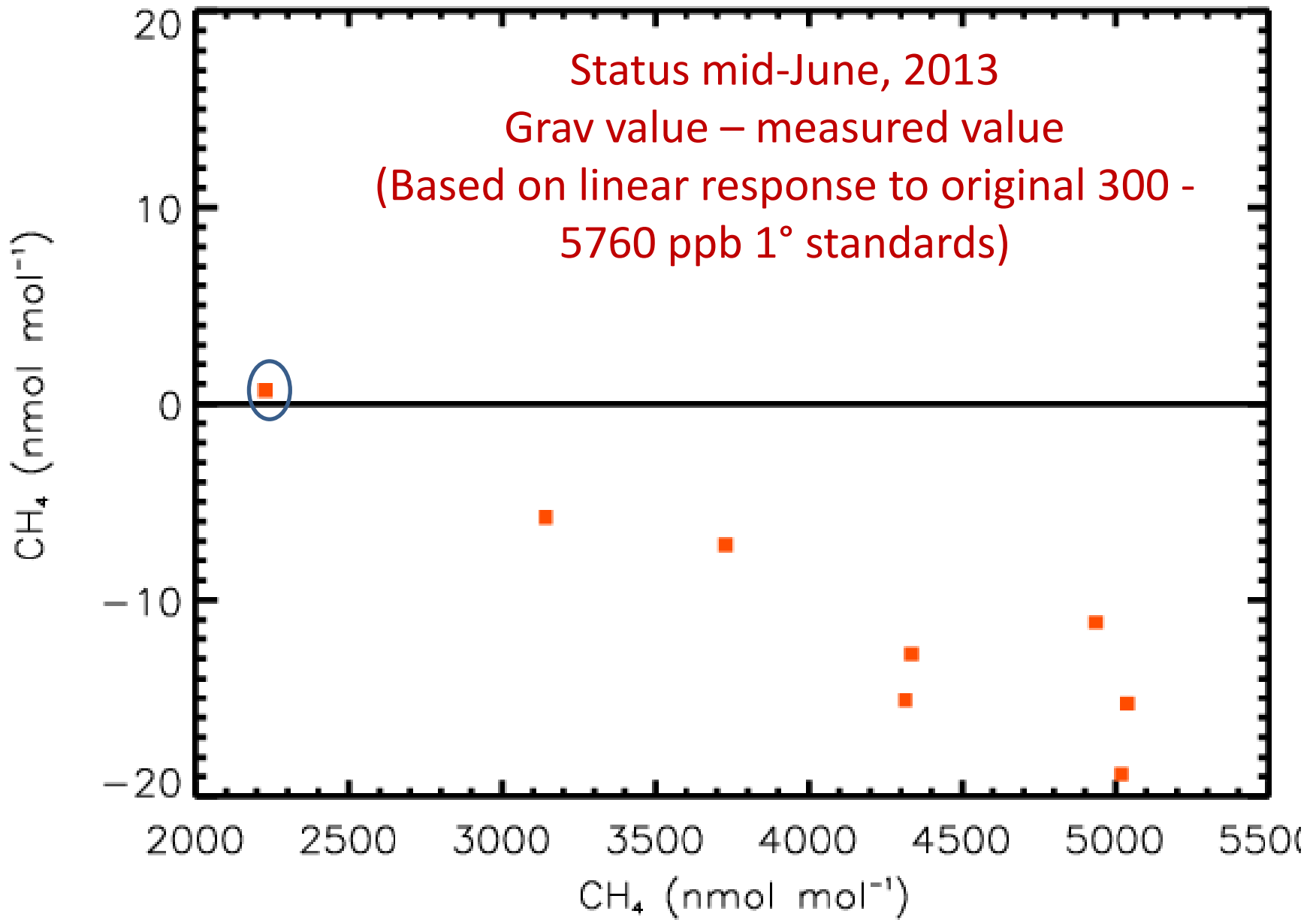
Source: Dlugokencky et al., JGR, doi:10.1029/2005JD006035, 2005.

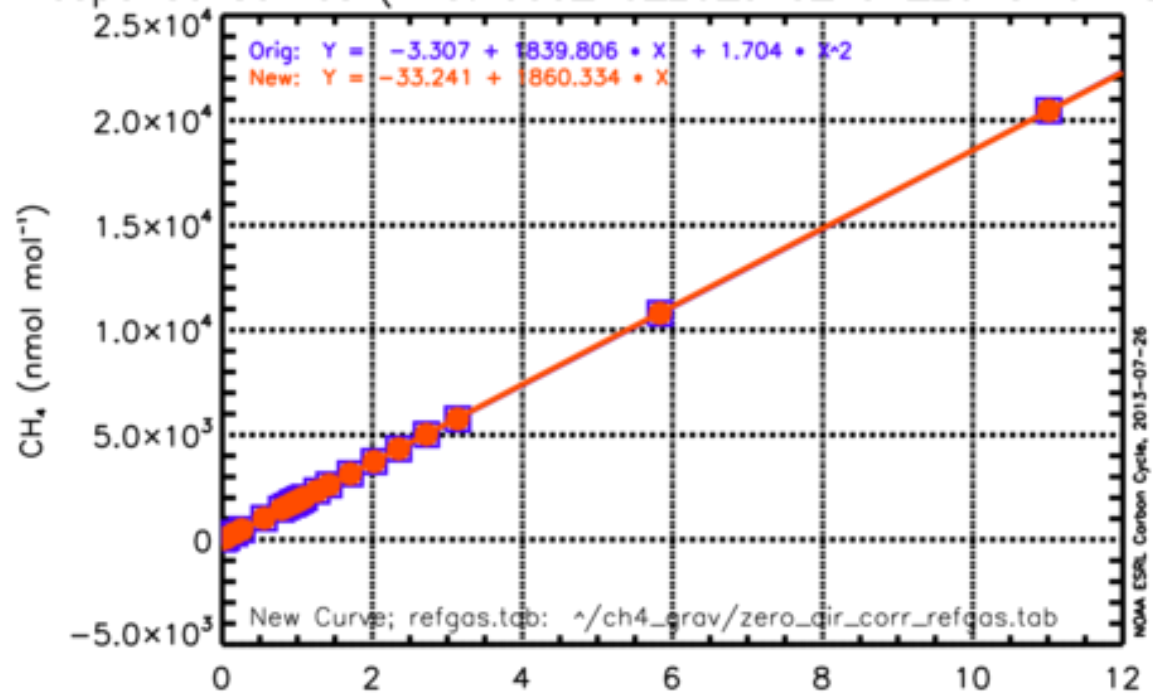
**AAL-18868**  
99.99%

Methane (Myers, Elkins, Hall)

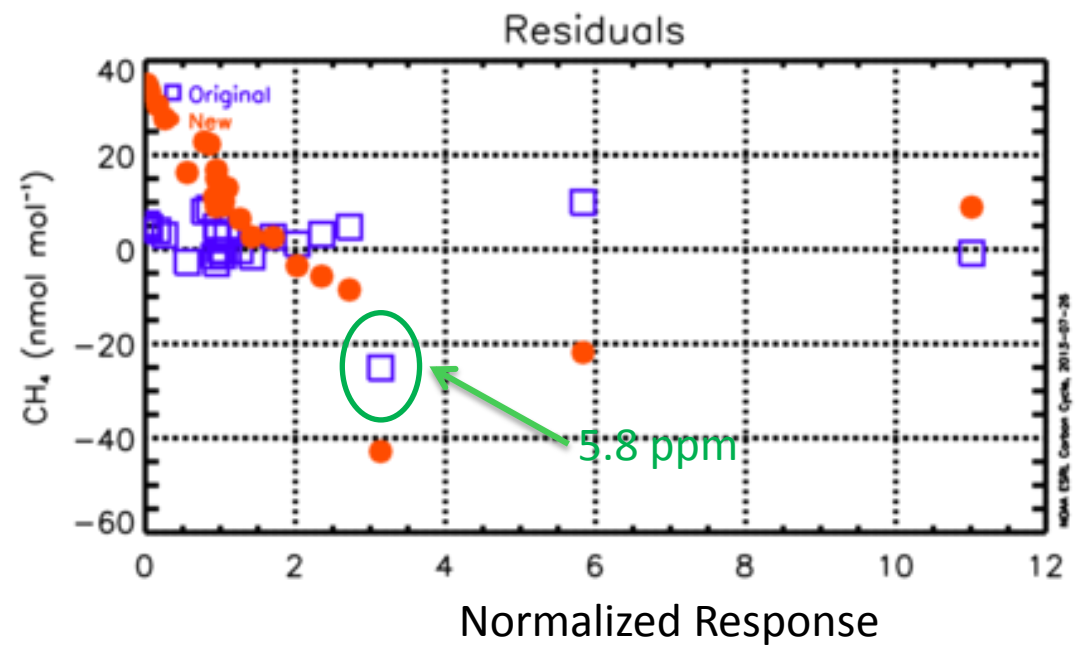
Yellow: Core range of WMO scale  
Green: Extended range





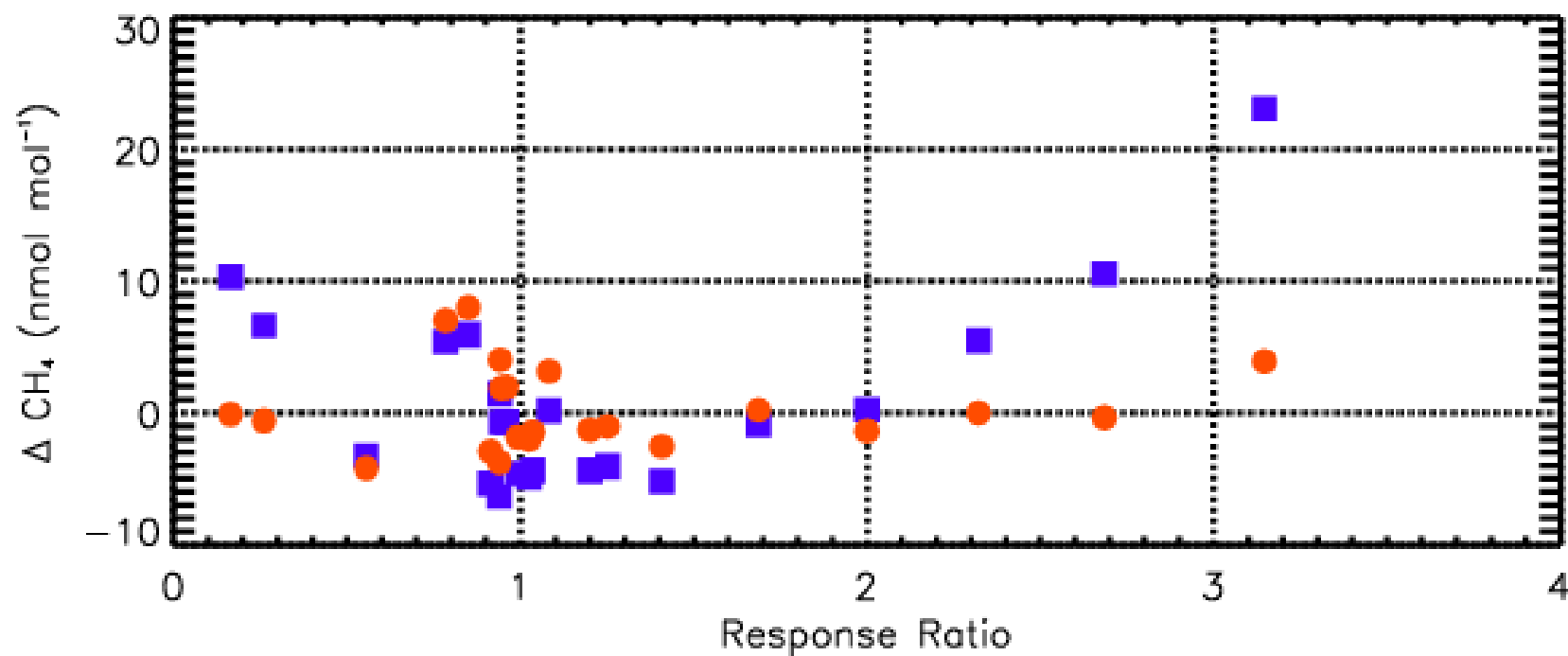
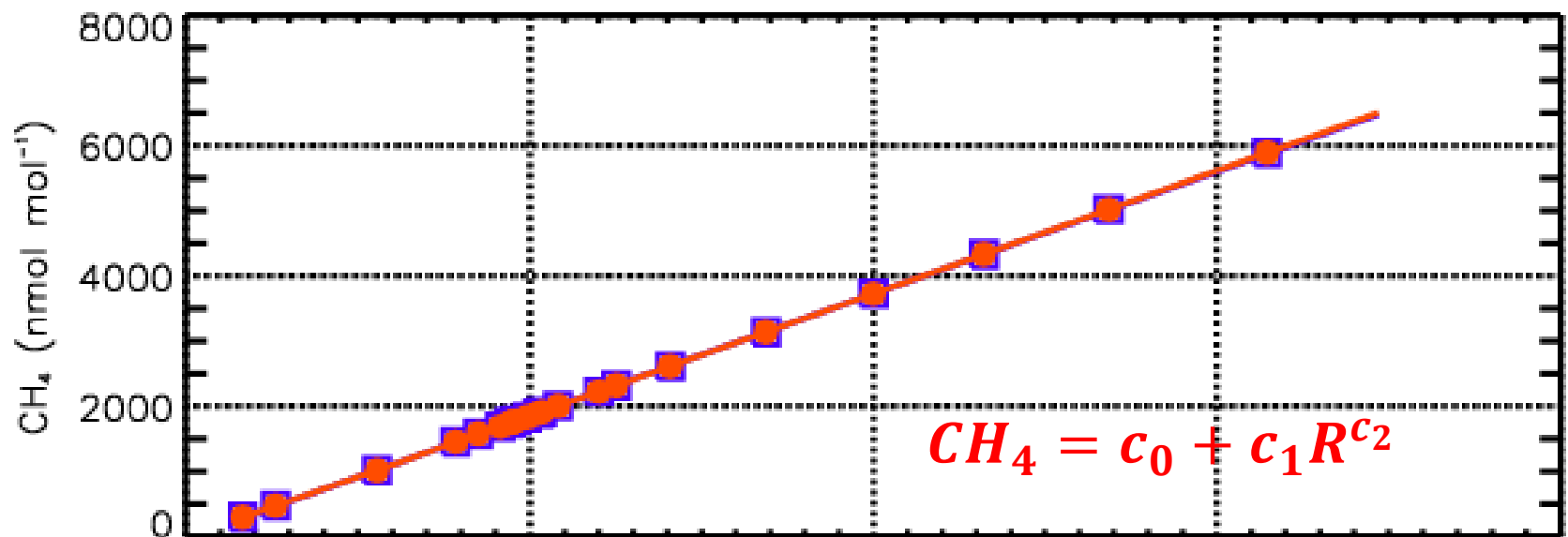


- Tested:
- Different transfer methods
  - Inclusion of 10 and 20 ppm standards
  - Original 5.8 ppm standard was not consistent with others



## 22 Primary Standards (X2004A)

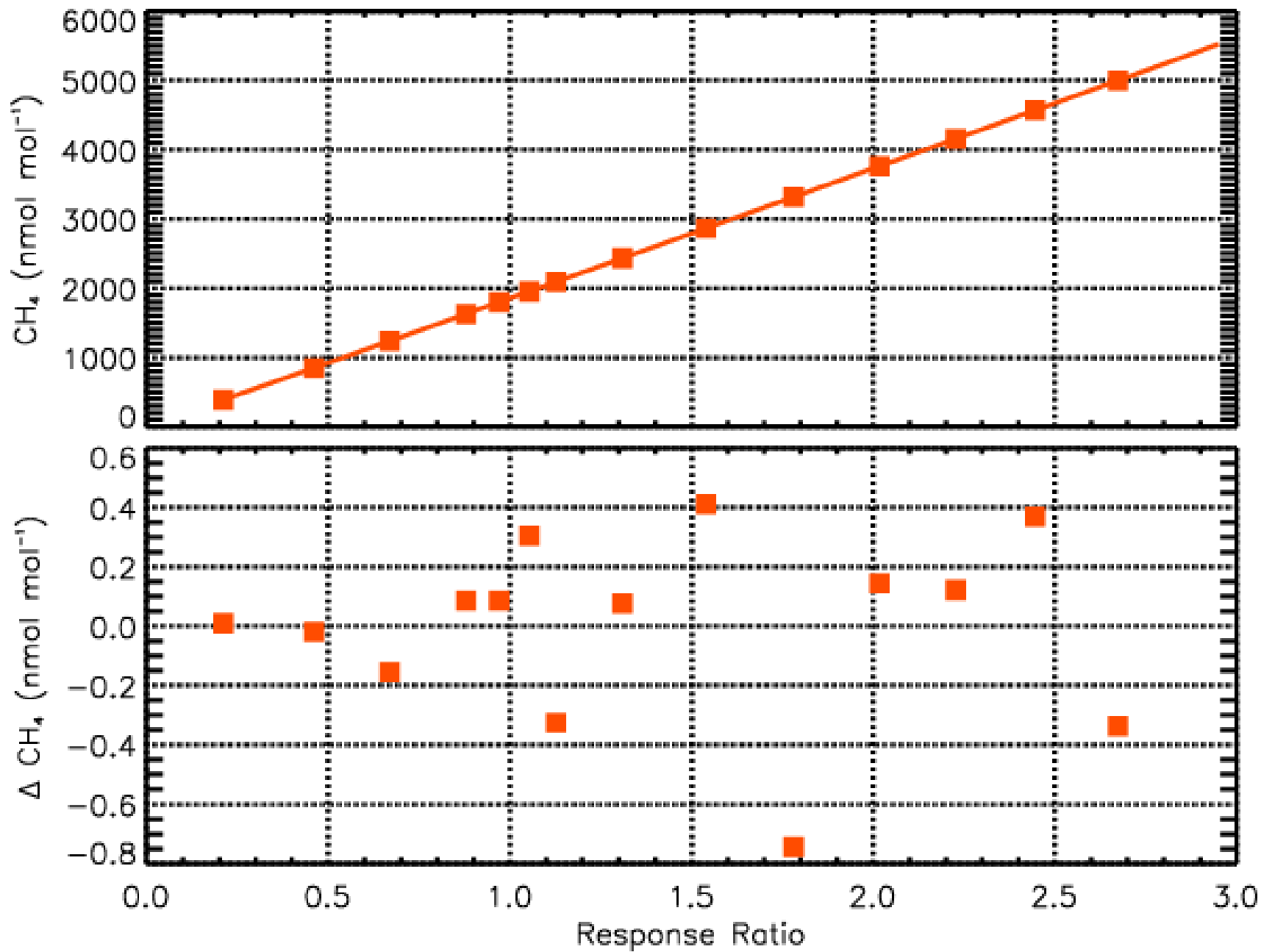
Cylinder ID	Year Prepared	Assigned CH <sub>4</sub> (ppb)	Uncertainty* (ppb)
FA01024	1995	302.3	2.0
FA01028	1994	478.3	2.1
FA01007	1995	1021.2	2.5
FF37050	1993	1457.6	2.5
FF37061	1993	1581.0	2.3
FF37040	1992	1690.1	2.3
FF37043	1993	1736.3	3.6
FF37052	1992	1748.1	2.3
FF37056	1993	1751.6	2.3
FF37045	1993	1780.6	2.2
FF37036	1991	1837.1	2.4
FA01017	1995	1896.3	2.4
FF37057	1992	1918.4	2.4
FF37024	1992	2010.5	2.3
FB03575	2013	2227.1	1.8
FF39454	1995	2322.4	2.6
FF39474	1995	2614.5	2.7
FF32820	2013	3140.4	2.0
FA02368	2013	3727.1	2.2
FF32783	2013	4334.0	2.5
FF32800	2013	5018.5	2.7
FB03568	2013	5893.6	3.6





# 14 Secondary Standards

Cylinder ID	Year Prepared	Assigned CH <sub>4</sub> (ppb)	Uncertainty (ppb) (68% CI)
CB09868	2013	389.3	0.3
CB09893	2013	849.5	0.3
CB09867	2013	1236.6	0.3
CB09898	2013	1626.7	0.3
CB09871	2013	1797.1	0.4
CB09891	2013	1952.4	0.5
CB09804	2013	2090.6	0.3
CB09888	2013	2433.5	0.4
CB09899	2013	2865.3	0.6
CB09900	2013	3317.5	0.4
CB09895	2013	3762.8	0.5
CB09889	2013	4155.1	0.8
CB08856	2013	4568.9	0.8
CB10121	2013	4998.0	1.0



# Recalibration of historical secondary standards

- All but 2 (of 21) archived in lab
- Measured 4X each, 3 GC and 1 CRDS
- Mean difference (2004A - 2004):  $-0.3 \pm 0.3$  ppb
- All calibrations since 17 July, 2013 use RC
  - Non-linearity greater since October, 2013
- Difference in tertiary standards (300-2600 ppb)
  - 1983 to September, 2013:  $-0.4 \pm 0.3$  ppb
  - October, 2013 to present:  $-0.4 \pm 1.9$  ppb

# Converting from X2004 to X2004A

- <http://www.esrl.noaa.gov/gmd/ccl/refgas.html>

## CH4 CALIBRATION SUMMARY FOR TANK # CA07949

CH<sub>4</sub> mixing ratios shown are on the WMO X2004A scale.

Reference:

*Conversion of NOAA CMDL Atmospheric Dry Air CH<sub>4</sub> Mole Fractions to a Gravimetrically Prepared Standard Scale,*

E.J. Dlugokencky, R. Myers, P. Lang, K. Masarie, A. Crotwell, K. Thoning, B. Hall, J. Elkins and L.P. Steele, *J. Geophys. Res.*, 110, D18306, doi:10.1029/2005JD006035.

Filling Code **A**

Date	Loc	Inst	Pressure	Value	S.D.	Num	Avg	Sdev
2008-01-24	BLD	H5	1920	1841.00	0.73	.		
2008-02-06	BLD	H5	1950	1840.98	0.80	.		
2008-12-17	BLD	H5	1950	1841.43	0.74	.		
2009-12-03	BLD	H5	2000	1840.94	0.65	.		
2010-07-06	BLD	H5	1900	1840.70	0.97	.		
2010-07-15	BLD	H5	1810	1841.27	0.90	.		
2010-08-06	BLD	H5	1820	1841.28	0.92	.		
2010-08-25	BLD	H5	1820	1840.76	0.72	.		
2011-01-25	BLD	H5	1420	1841.16	1.13	.		
2011-12-08	BLD	H5	660	1841.01	0.47	.		
2012-05-02	BLD	H5	240	1841.34	0.74	.		
2012-06-22	BLD	H5	210	1841.35	0.60	.		
2014-10-20	BLD	H5	250	1841.42	0.53	.		
2014-12-23	BLD	H5	300	1841.32	0.85	.		
2015-03-20	BLD	H5	350	1841.15	0.42	.		

# CH<sub>4</sub>: Summary and Conclusions

- Transitioned from X2004 to X2004A scales
  - Expand scale with new gravs at 2200 to 5900 ppb
- New secondary standards (390 to 5000 ppb)
  - Assigned values based on 6 response curves from primary standards
  - Non-linear response: modeled as power function
- All historical secondary standards reassigned
  - Changes propagated to all calibrations from 1983 to present