Do we need the WMO Mole Fraction Scales for CO2 and other greenhouse gases?

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Requirements for our greenhouse gas measurements

Goals: 1. Provide independent assessment of emissions reductions
2. Monitor & understand the carbon cycle, improve prognoses

Measurements should be accepted as fully trustworthy, implying complete and prompt disclosure of all results, including data flagged as "bad"

Note 1: Disclosure is not an afterthought. It takes people and resources

Data should be able to stand up to challenges of its comparability.

Measurements should meet the stated WMO goals for comparability

All reported measurements should be accompanied by defensible uncertainty estimates.

Note 1: Defensible uncertainty estimates require a considerable amount of duplication of actual air samples.

Note 2: Uncertainty includes varying systematic errors that are poorly understood

Requirements for our greenhouse gas measurements

Some definitions in metrology:

Measurement: Process of experimentally obtaining a quantity value that can reasonably attributed to a quantity
Note: Any measurement is a comparison with a measurement standard

Measurand: Quantity *intended* to be measured
Note: A measurement includes the collection of a sample and its pretreatment, such as drying.

Measurement result: Set of quantity values attributed to a measurand, together with any other available relevant information
Note: In most cases a measurement result has to include an estimate of its uncertainty, taking into account all known contributions, not just a statistical estimate of repeatability.

Measurement error: Measured quantity value minus a reference quantity value

Measurement precision: Closeness of agreement of replicate measurements under specified conditions:
1. repeatability: same operators, same equipment and procedure, same location, same conditions, over relatively short time
2. reproducibility: different operators, equipment, procedure, location, conditions, and over extended time period.

Comparability: Measurement results are comparable if they are metrologically traceable to the same reference

Traceability: result is related to a reference through a documented unbroken *chain* of calibrations

Sources: VIM3 (2008); De Bièvre, Metrologia, 2008

Bureau International des Poids et Mesures

Key comparison of CO_2 in synthetic air - CCQM K52 (2006)

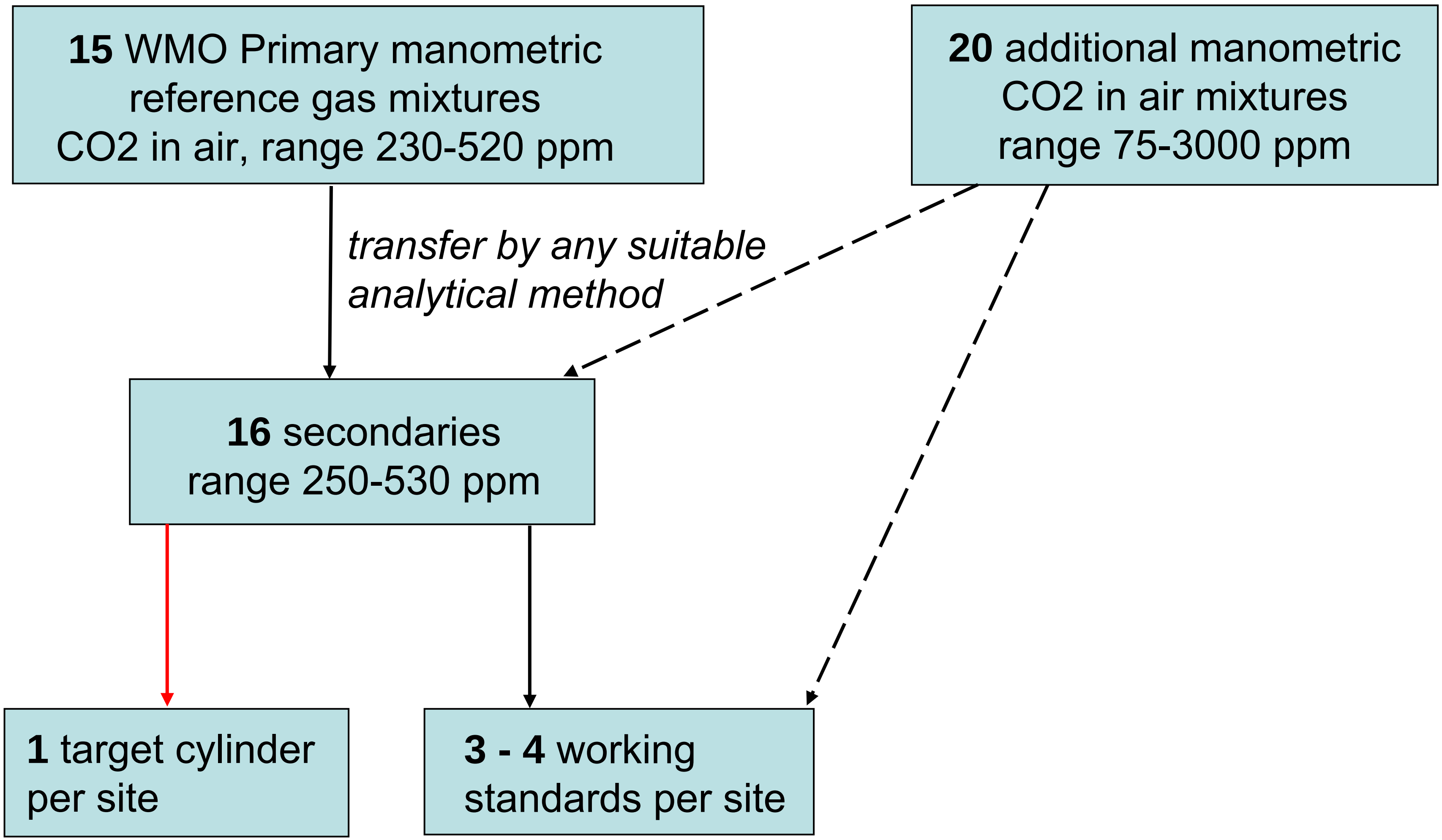
Nominal value: 360 µmol/mol CO_2 in N_2, O_2 mixture.

	diff (µmol/mol)	2σ (µmol/mol)
NMi VSL (Netherlands)	-0.17	±0.36
Inmetro (Brazil)	0.82	3.6
NMIA (Australia)	-0.22	0.70
CEM (Spain)	-0.29	0.73
NPL (UK)	0.21	0.44
SMU (Slovak Rep.)	0.74	1.2
NMIJ (Japan)	0.20	0.48
CERI (Japan)	-0.47	0.61
CENAM (Mexico)	-2.31	2.2
NMI-SA (South Africa)	0.90	3.9
NIST (US)	-0.31	0.34
INRiM (Italy)	0.57	0.90
NPLI (India)	-6.04	13.6
BAM (Germany)	-0.22	2.9
VNIM (Russia)	-0.09	0.7
LNE (France)	-0.58	1.2
NIM (PR China)	0.26	1.1
KRISS (S. Korea)	0.08	0.06

http://kcdb.bipm.org/AppendixB/

Where are we now?

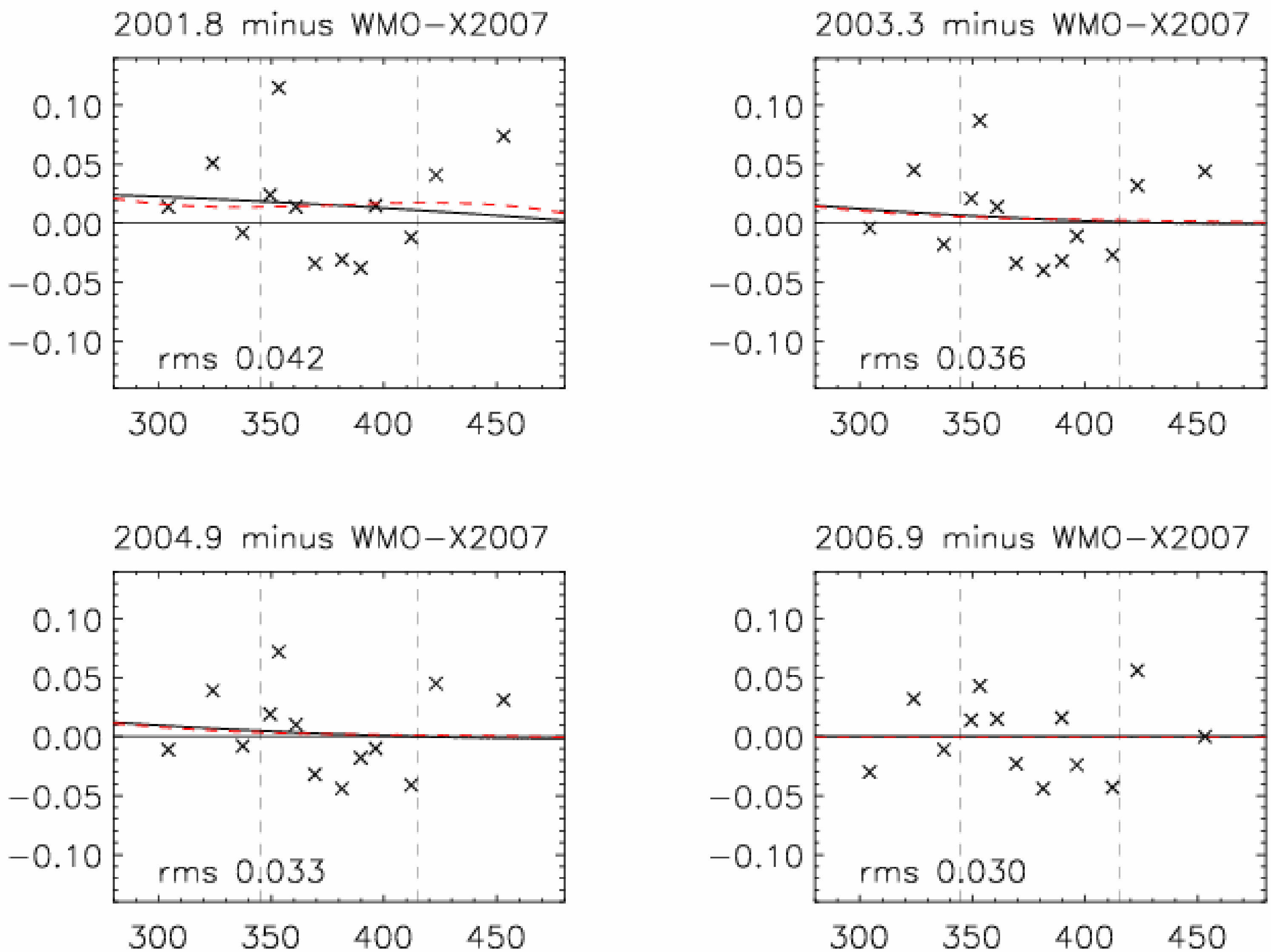
Propagation of WMO Mole Fraction Scale for CO2



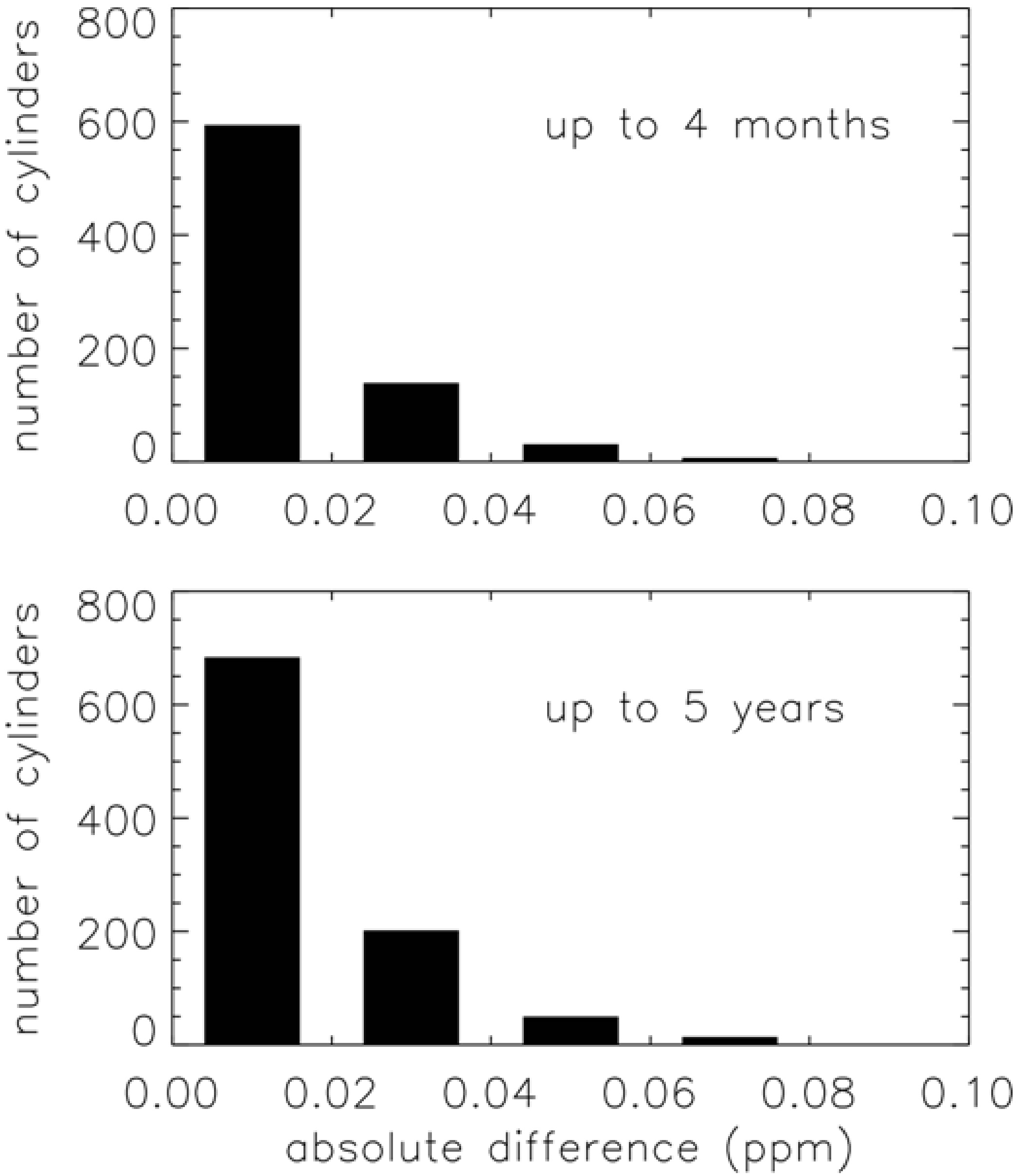
Standard deviation of individual cylinder manometric calibrations during each calibration episode.

	N	St.Dev. (all) ppm	St.Dev. (300-420) ppm (one sigma)
1996	64	0.12	0.09
1998	58	0.14	0.13
2000	55	0.11	0.10
2001	62	0.09	0.08
2003	62	0.06	0.06
2004	48	0.04	0.04
2006	41	0.03	0.03

recent history of the WMO scale



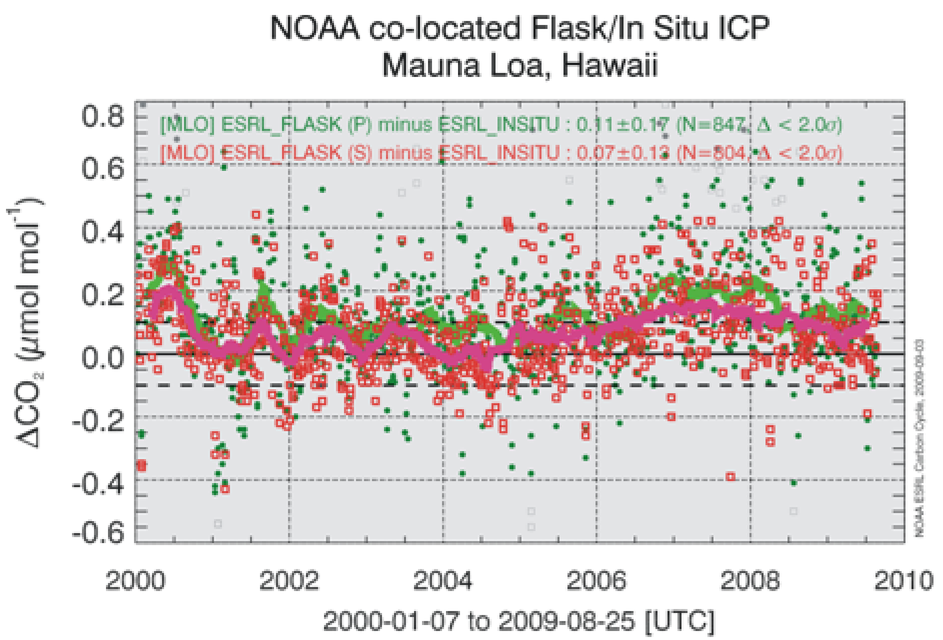
Where are we now?

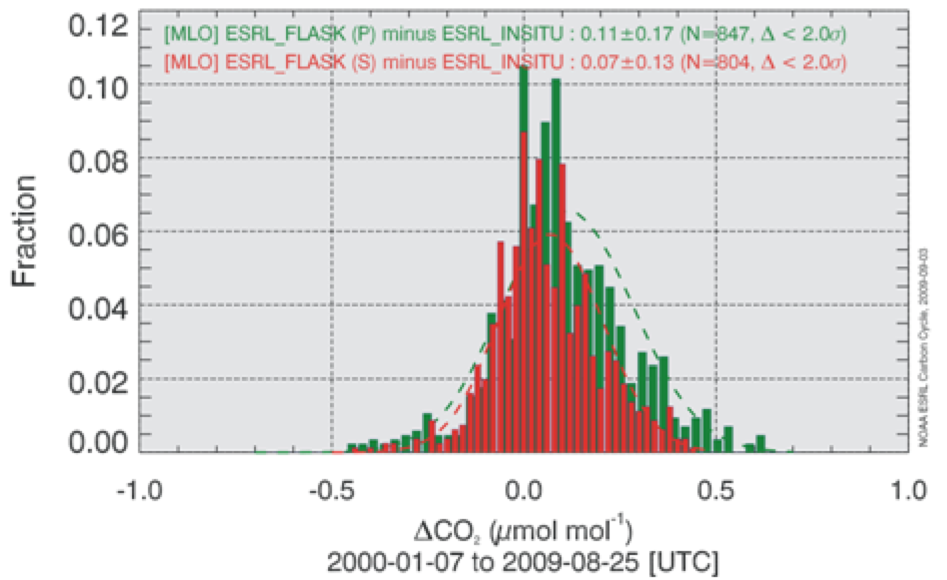


771 comparisons
mean absolute difference
0.015 ppm

950 comparisons
mean absolute difference
0.016 ppm

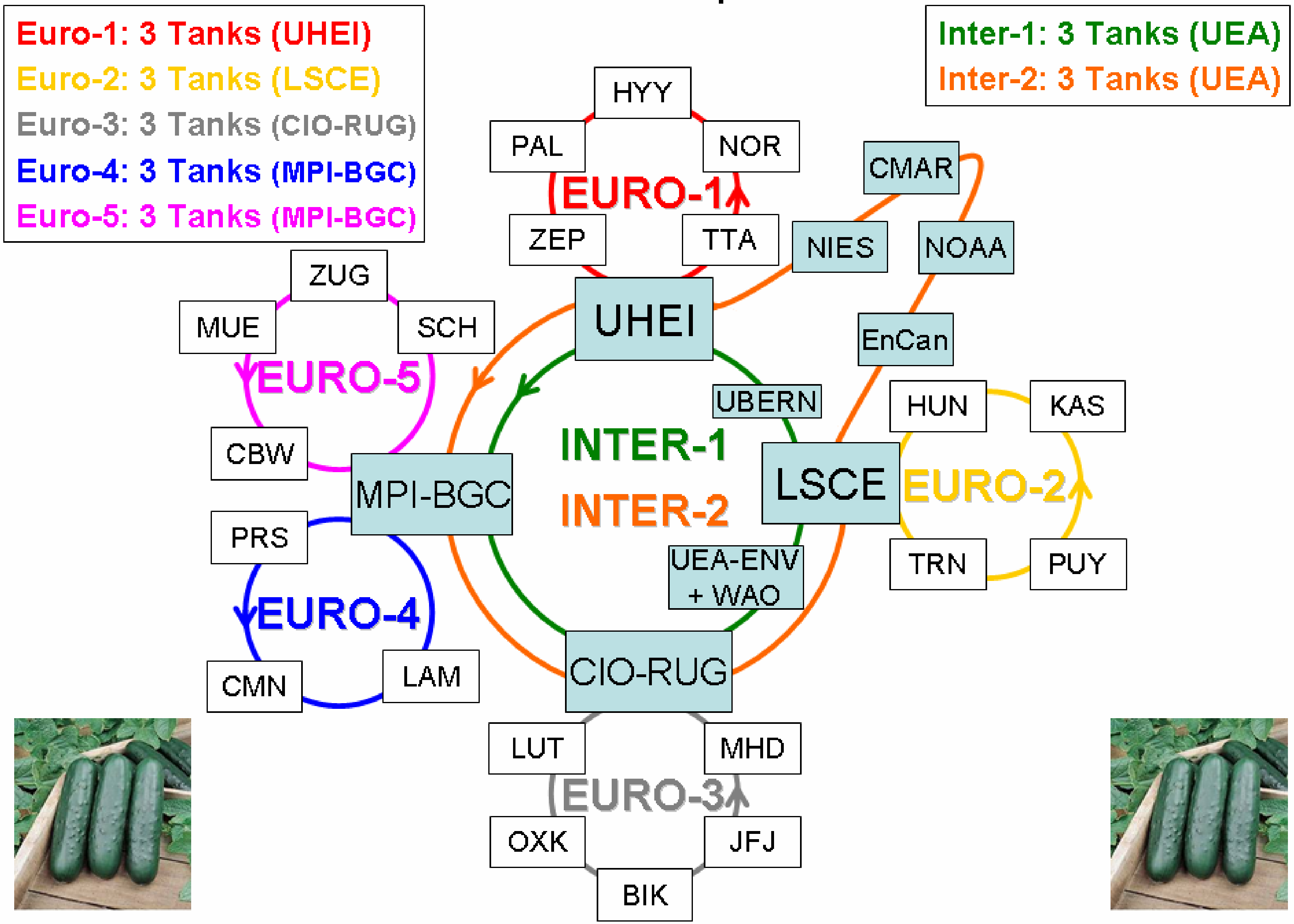
Where are we now?



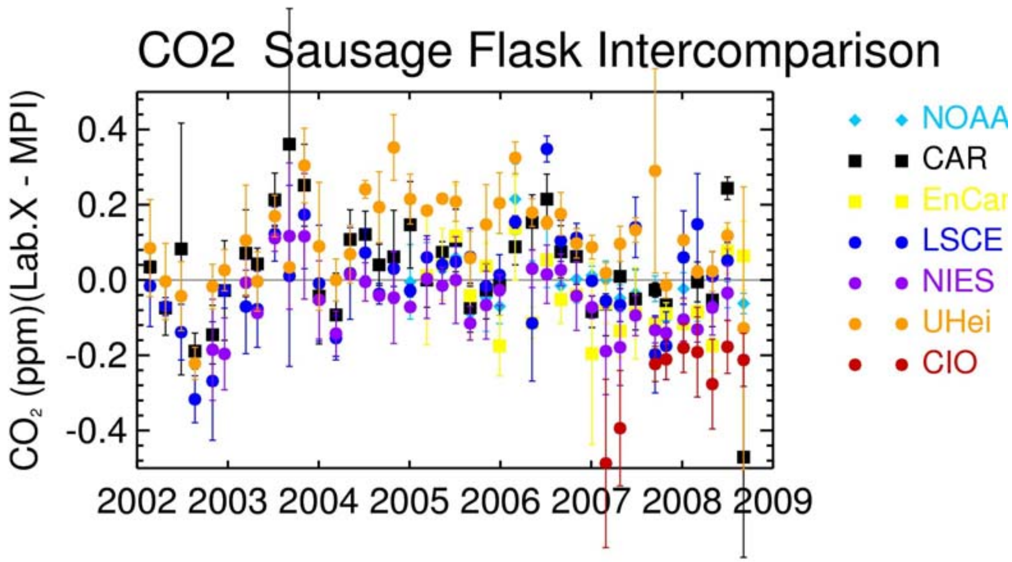


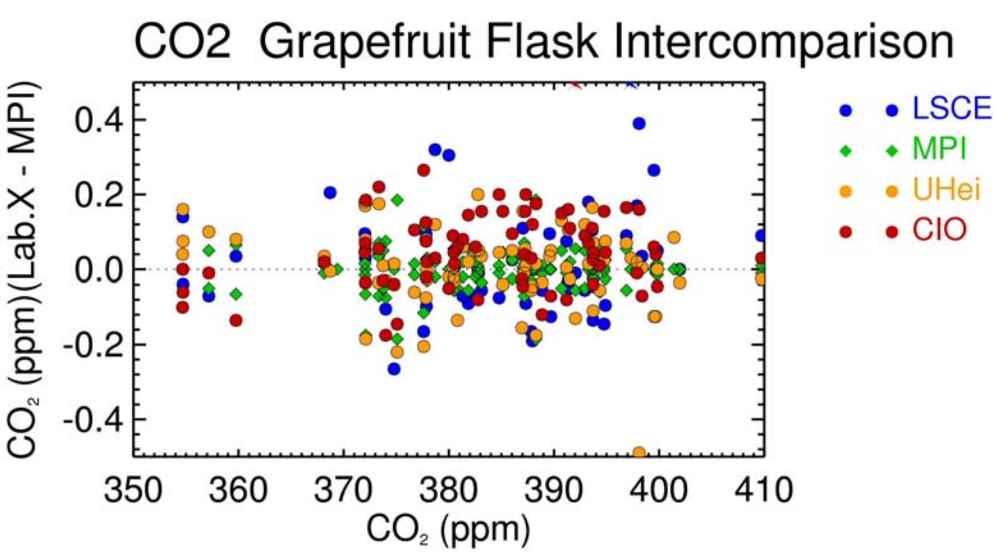
Where are we now?

Circulation of CarboEurope ICP Cucumbers



Where are we now?





Proposed recommendations

Each participant in the WMO GAW network for greenhouse gases maintains traceability to the WMO mole fraction scale for each gas:

- Single, well defined, traceability chain to WMO.
- Target gases provide information values.
- Comparisons between labs provide information values.

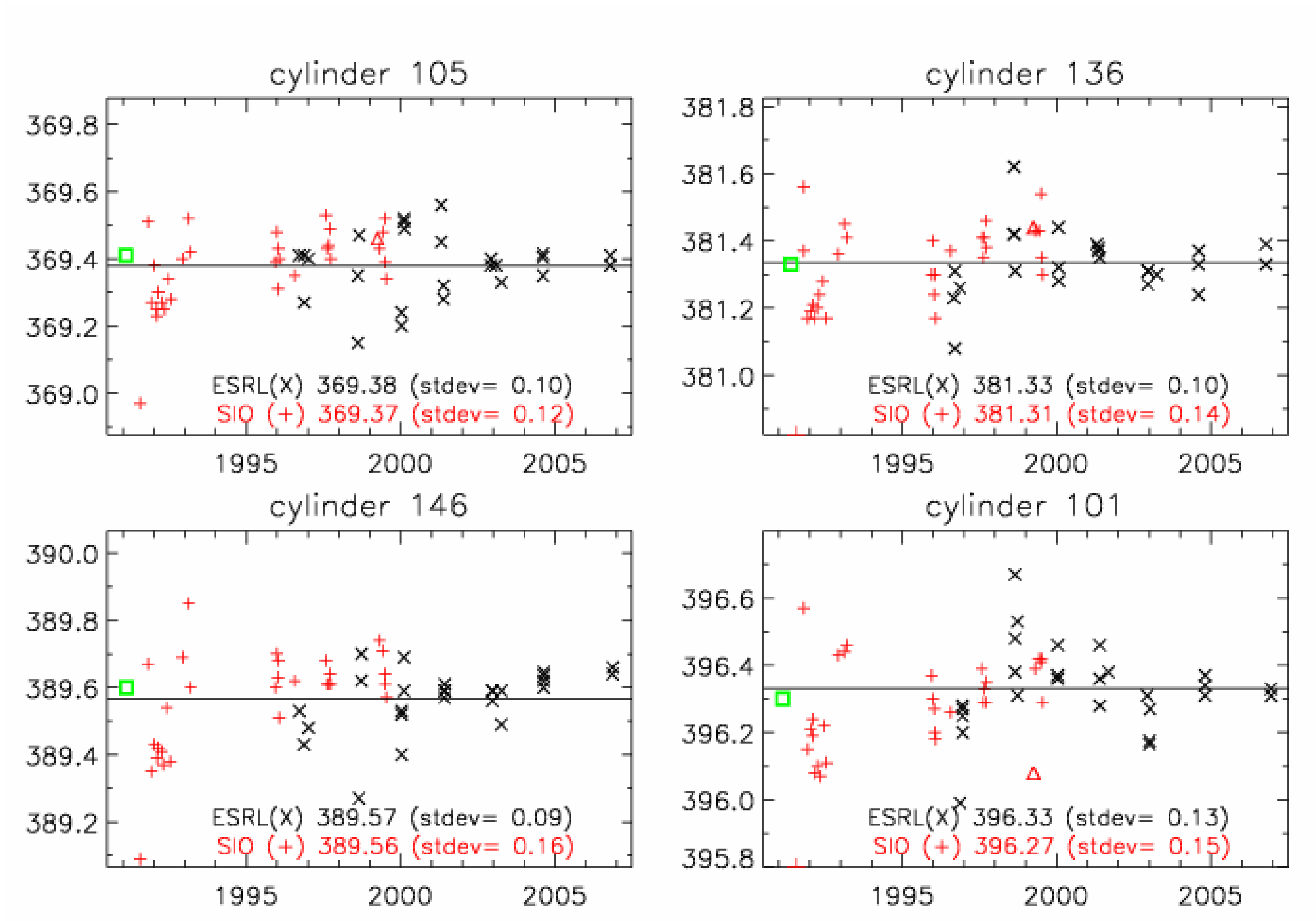
ALL measurement results include well documented full uncertainty resulting from:

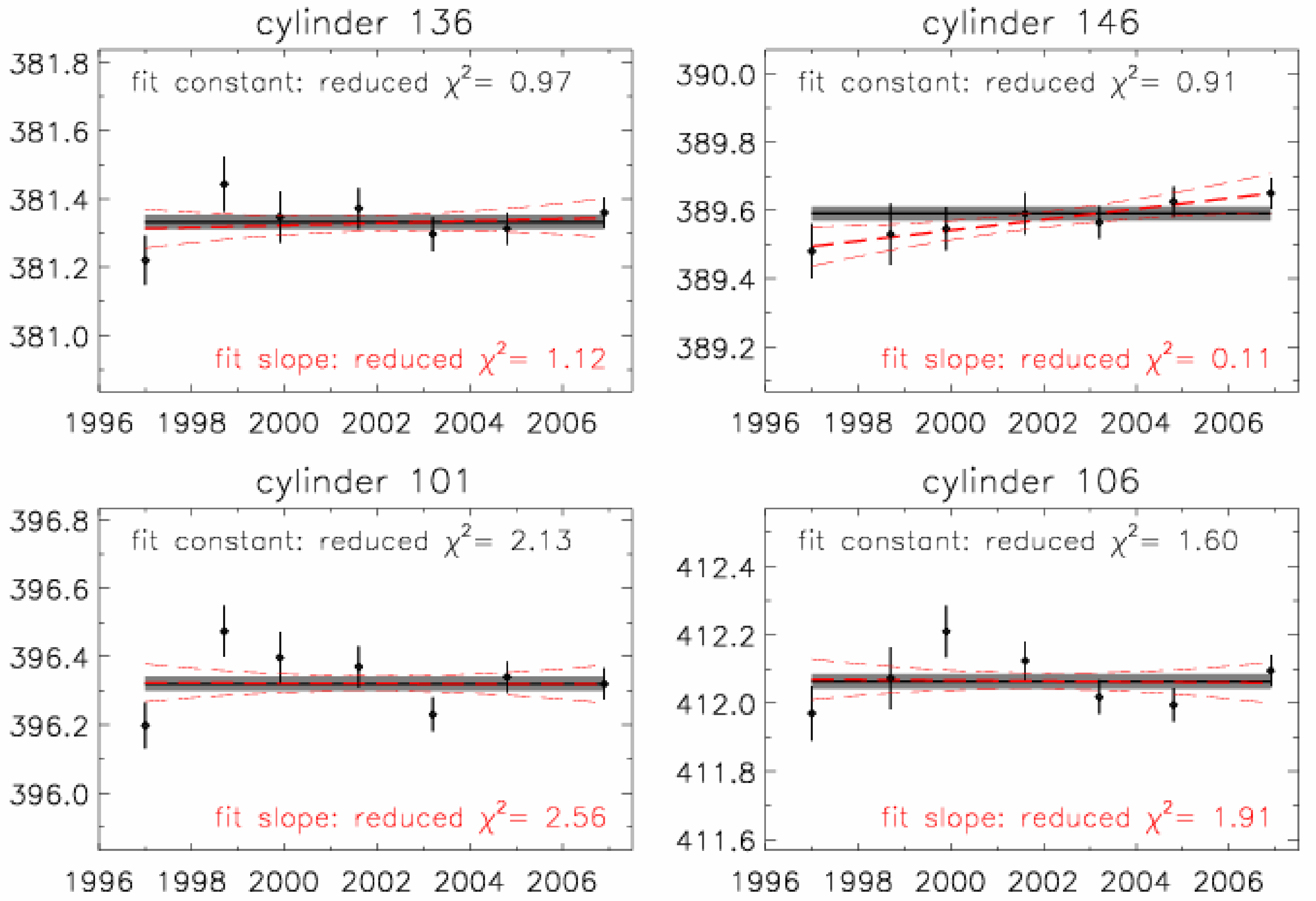
- Transfer of the calibration scale (not uncertainty of scale itself)
- Repeatability of the measurement
- Slow and varying biases that are typically present, e.g. due to air handling
- Other relevant factors

Ongoing comparisons of actual samples, incl. near-real time disclosure, with other labs for ongoing quality control

Full disclosure to general public within a year

calibrations of 15 WMO Primaries

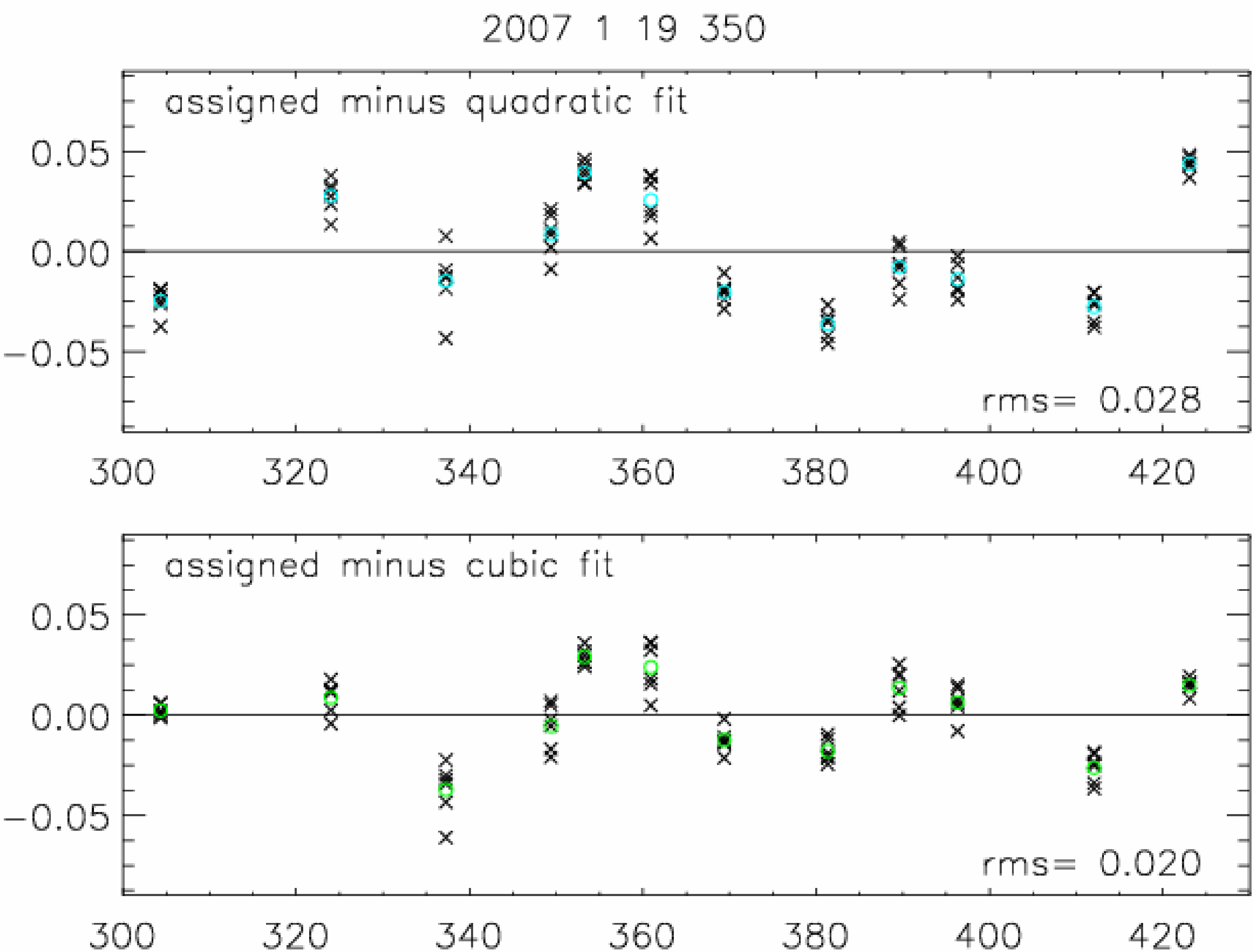


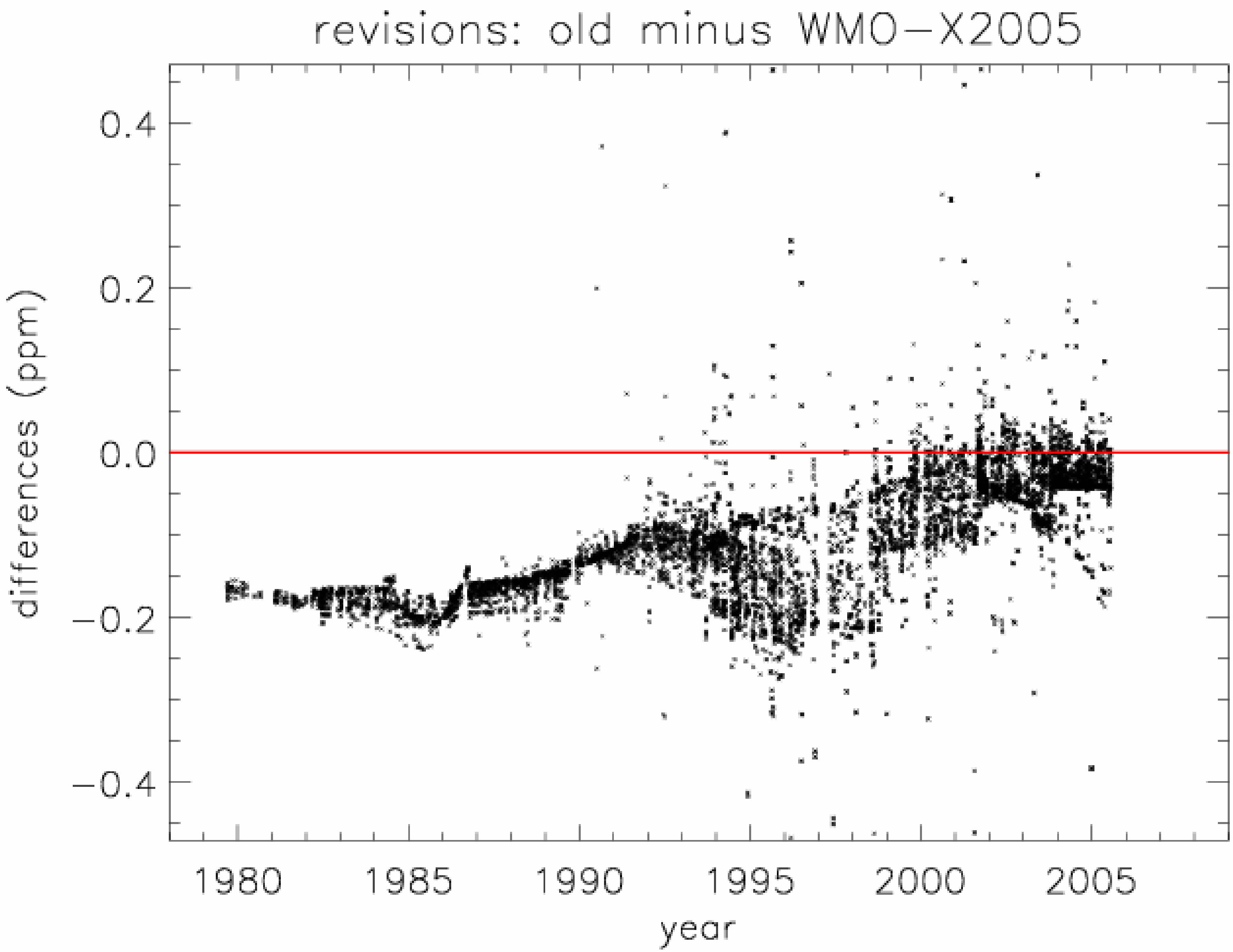

cylinder 136
fit constant: reduced χ^2= 0.97
fit slope: reduced χ^2= 1.12
381.8
381.6
381.4
381.2
381.0
cylinder 146
fit constant: reduced χ^2= 0.91
fit slope: reduced χ^2= 0.11
390.0
389.8
389.6
389.4
389.2
cylinder 101
fit constant: reduced χ^2= 2.13
fit slope: reduced χ^2= 2.56
396.8
396.6
396.4
396.2
396.0
cylinder 106
fit constant: reduced χ^2= 1.60
fit slope: reduced χ^2= 1.91
412.4
412.2
412.0
411.8
411.6
1996
1998
2000
2002
2004
2006

Comparison of NIES gravimetric standards with WMO-X2005

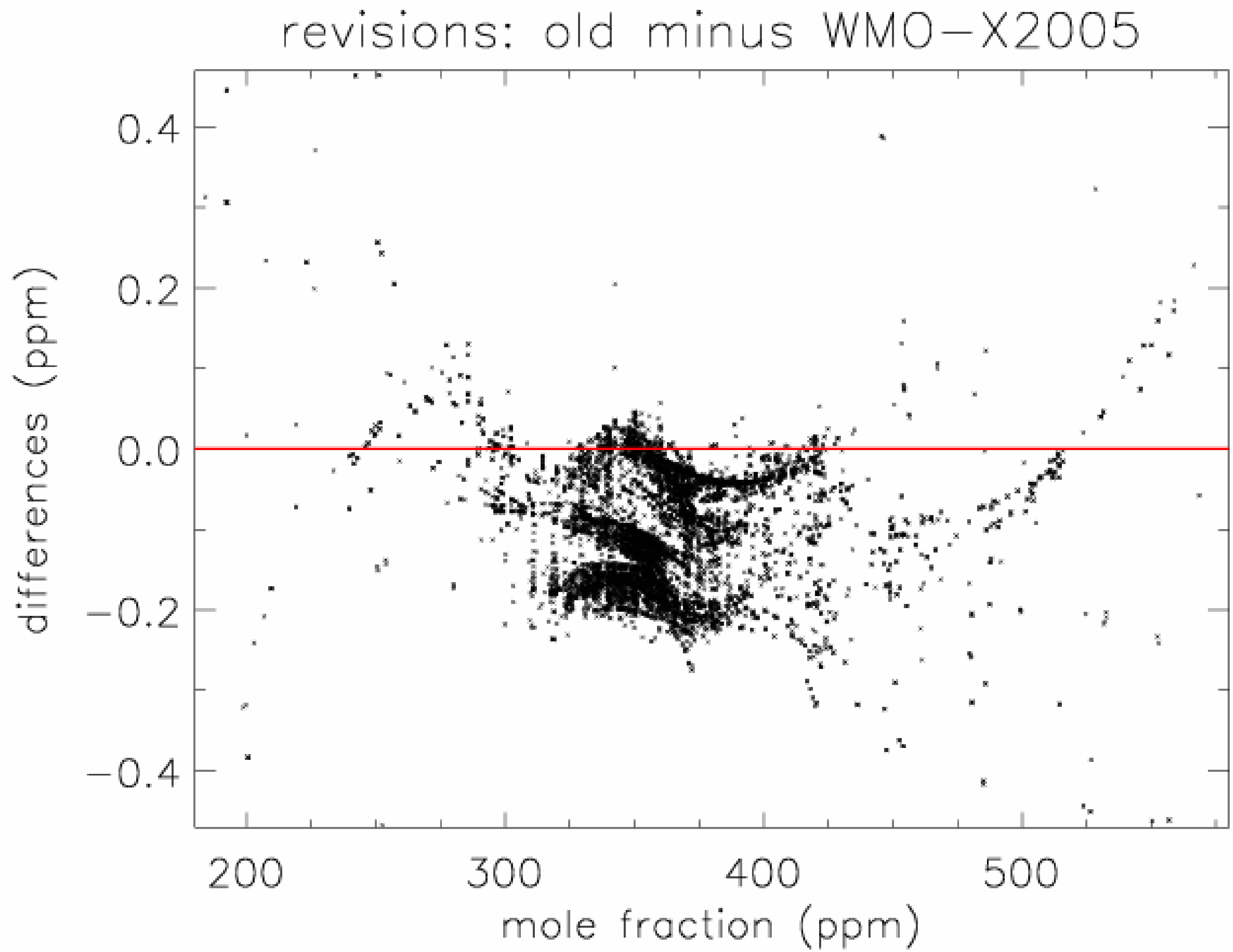
Cylinder	NIES	ESRL NDIR May 05 July 06	ESRL mano July 06
30089	350.14	350.21	350.15
30091	350.02	350.03	350.03
30092	390.11	390.09	390.10
30093	390.11	390.09	390.15
30094	389.03	389.02	389.02

NIES data courtesy of Yasunori Tohjima

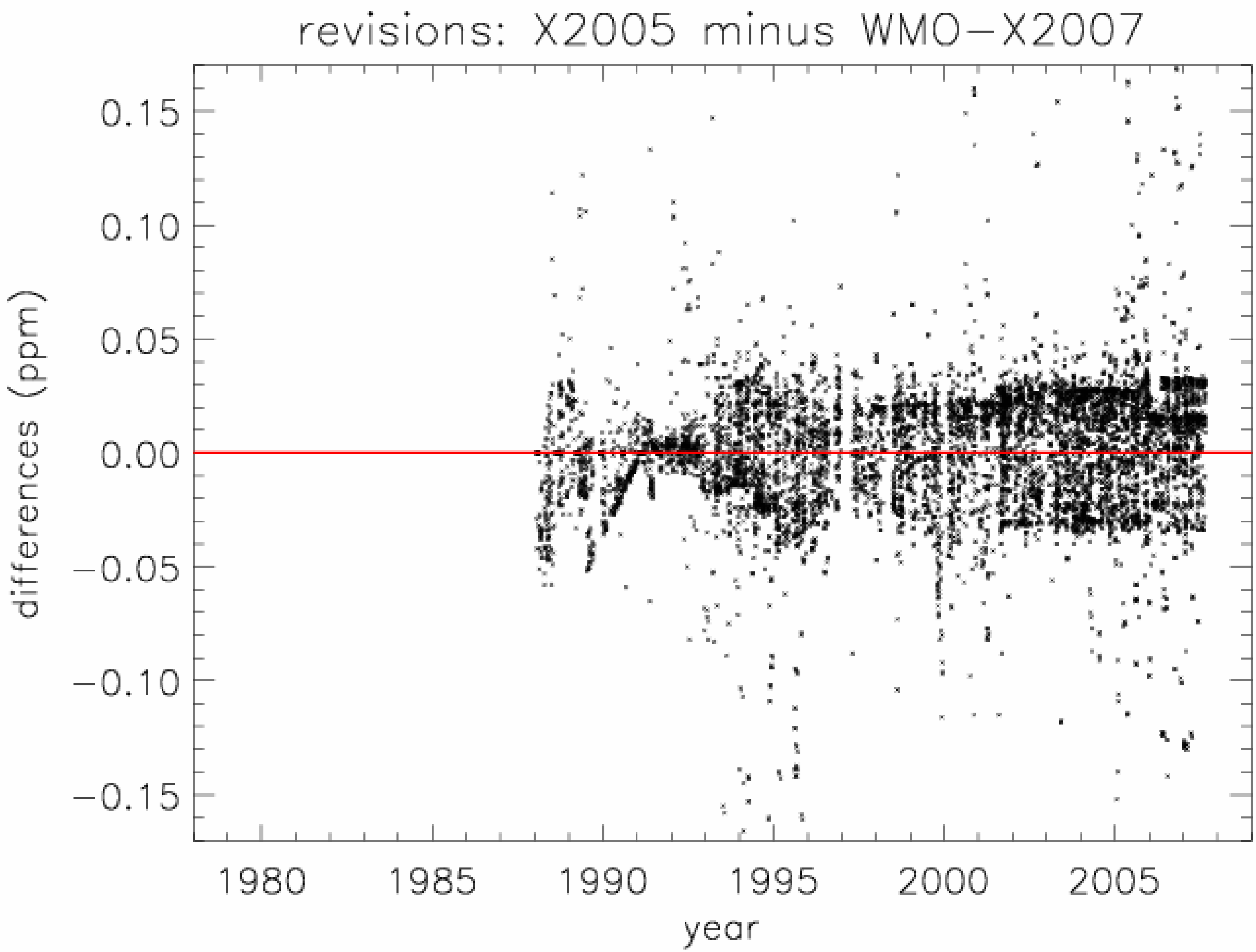

2007 1 19 350
assigned minus quadratic fit
rms= 0.028
0.05
0.00
−0.05
300
320
340
360
380
400
420
assigned minus cubic fit
rms= 0.020
0.05
0.00
−0.05
300
320
340
360
380
400
420

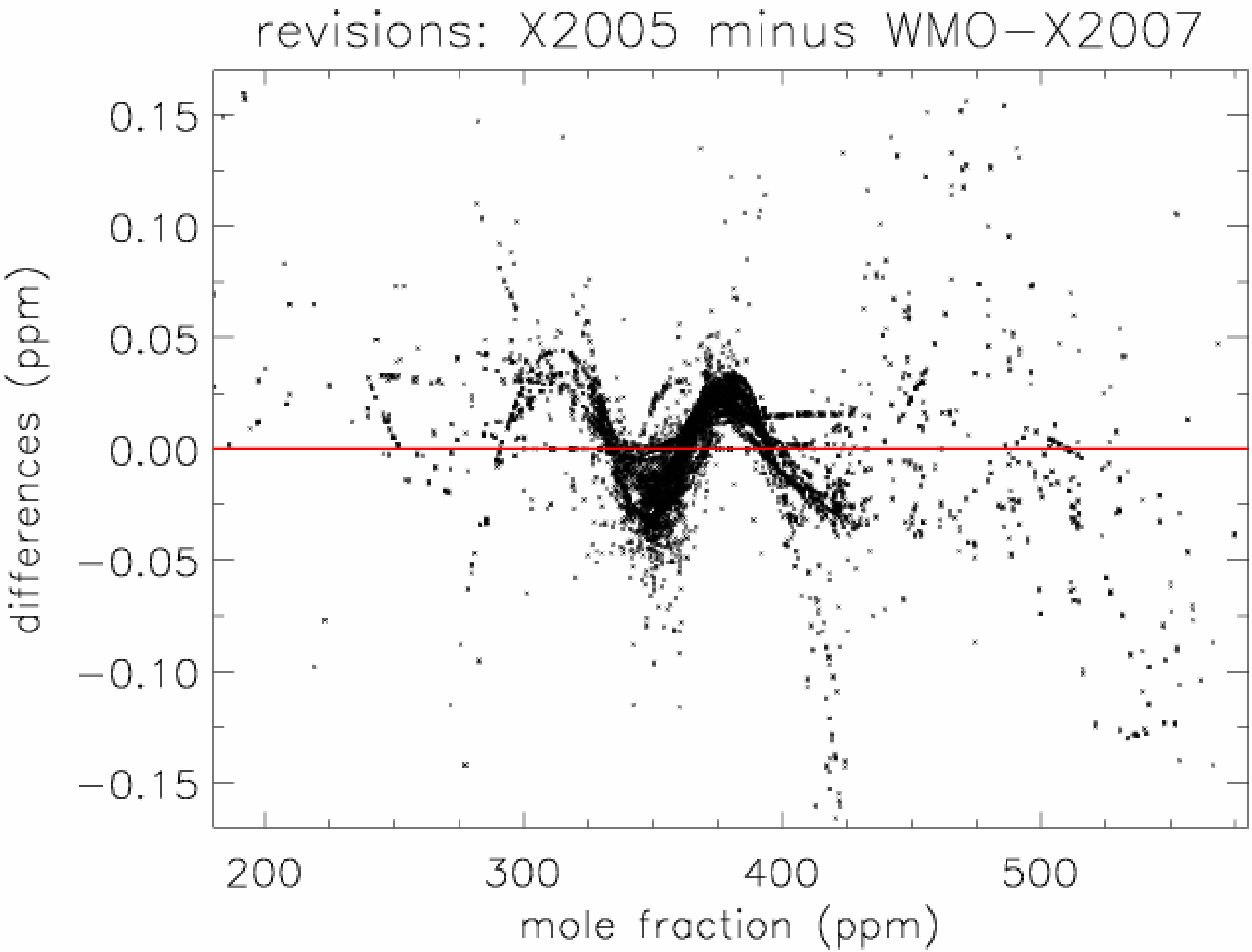


revisions: old minus WMO−X2005
differences (ppm)
0.4
0.2
0.0
−0.2
−0.4
1980
1985
1990
1995
2000
2005
year



revisions: old minus WMO-X2005
differences (ppm)
0.4
0.2
0.0
−0.2
−0.4
200
300
400
500
mole fraction (ppm)


revisions: X2005 minus WMO−X2007
differences (ppm)
0.15
0.10
0.05
0.00
−0.05
−0.10
−0.15
1980
1985
1990
1995
2000
2005
year


revisions: X2005 minus WMO−X2007
differences (ppm)
0.15
0.10
0.05
0.00
−0.05
−0.10
−0.15
200
300
400
500
mole fraction (ppm)

www.esrl.noaa.gov/gmd/dv/ccg/refgas/

SRL Global Monitoring Division - Mozilla Firefox <2>

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Visualization
Greenhouse Gases
Trace Gases
South Pole Ozone Hole
Solar Radiation
US Surface Radiation
Atmospheric Transport

Data Information

Observation Sites

Data Access

Anonymous FTP Data

Submit

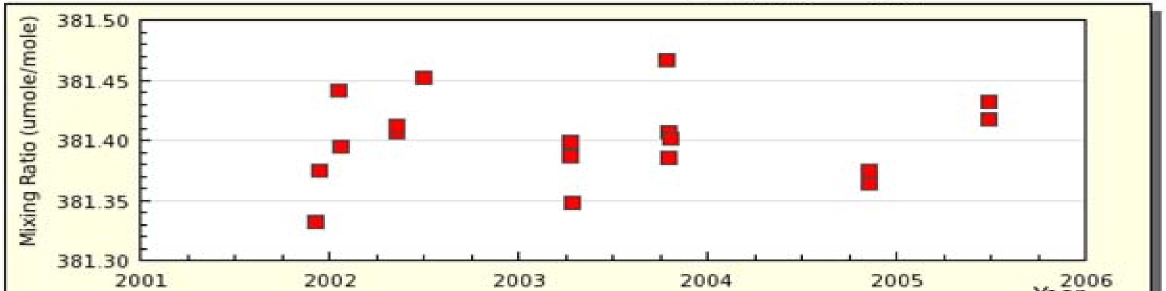
* denotes required field

Search for serial number

CO2 CALIBRATION SUMMARY FOR TANK # ca04969

Filling Code **A**

DATE	LOC	INST	PRESS	CONC.	S.D.		NUM	AVG	SDEV
2001-12-05	BLD	L3	2000	381.332	0.035	.			
2001-12-14	BLD	L3	2000	381.374	0.030	.			
2002-01-18	BLD	L3	2000	381.442	0.007	.			
2002-01-22	BLD	L3	2000	381.395	0.058	.			
2002-05-10	BLD	L3	2000	381.407	0.007	.			
2002-05-13	BLD	L3	2000	381.412	0.010	.			
2002-05-20	BLD	L3	2000	396.953	0.008	*			
2002-07-02	BLD	L3	2000	381.452	0.022	.			
2003-04-10	BLD	L3	1650	381.387	0.013	.			
2003-04-11	BLD	L3	1650	381.399	0.004	.			
2003-04-14	BLD	L3	1650	381.348	0.038	.			
2003-10-16	BLD	L3	1300	381.467	0.063	.			
2003-10-17	BLD	L3	1300	381.407	0.020	.			
2003-10-20	BLD	L3	1300	381.385	0.013	.			
2003-10-22	BLD	L3	1300	381.401	0.004	.			
2004-11-08	BLD	S5	750	381.371	0.005	.			
2004-11-09	BLD	S5	750	381.375	0.009	.			
2004-11-10	BLD	S5	750	381.364	0.010	.			
2005-06-29	BLD	S5	400	381.432	0.020	.			
2005-06-30	BLD	S5	400	381.417	0.015	.			
							19	381.40	0.03



Some limits of calibration transfer standards