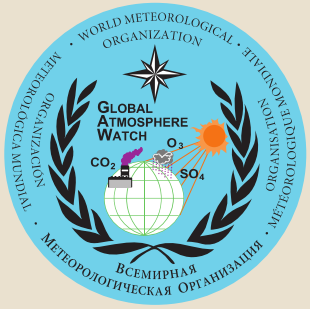

WMO/GAW Standard Gases and Scales for Greenhouse Gases

SUDA Kazuto

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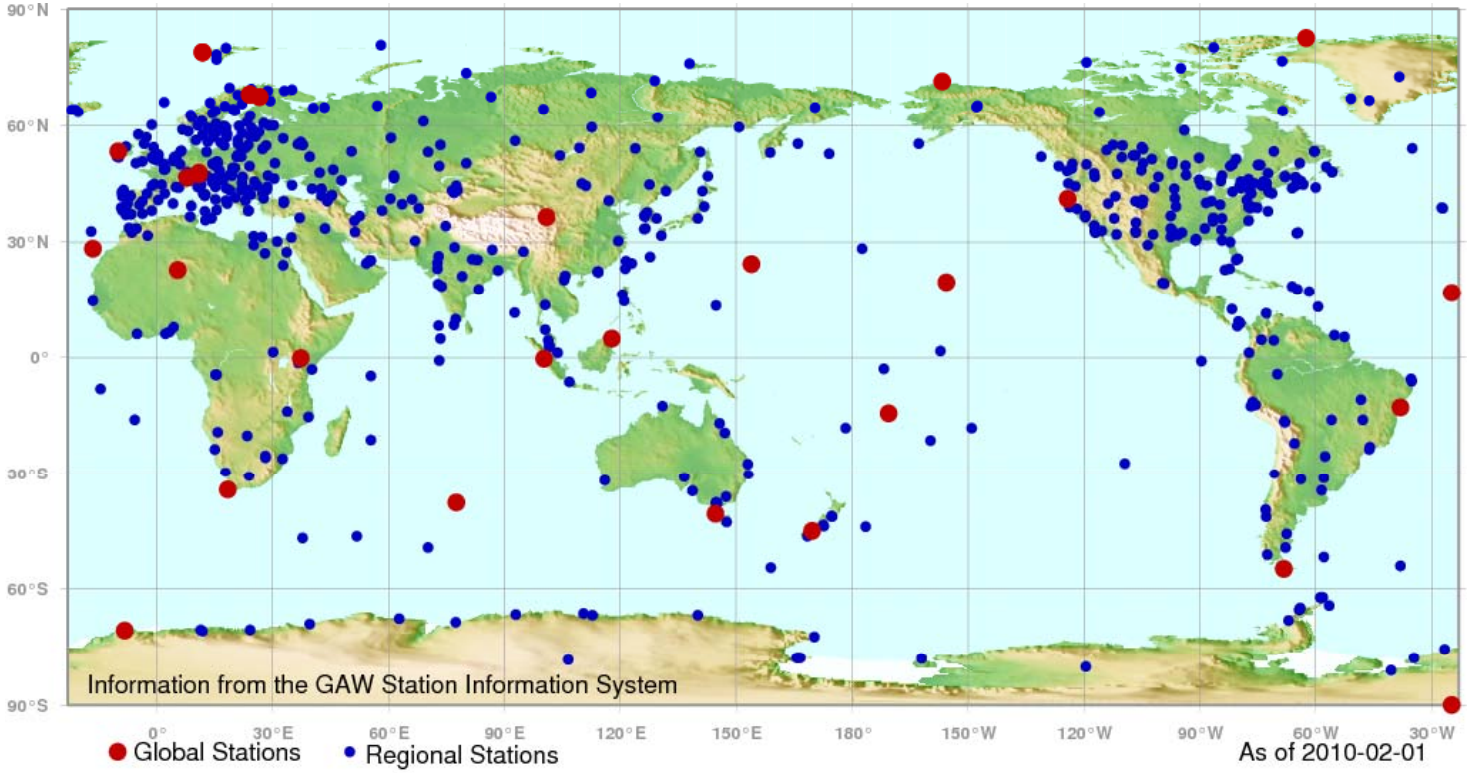
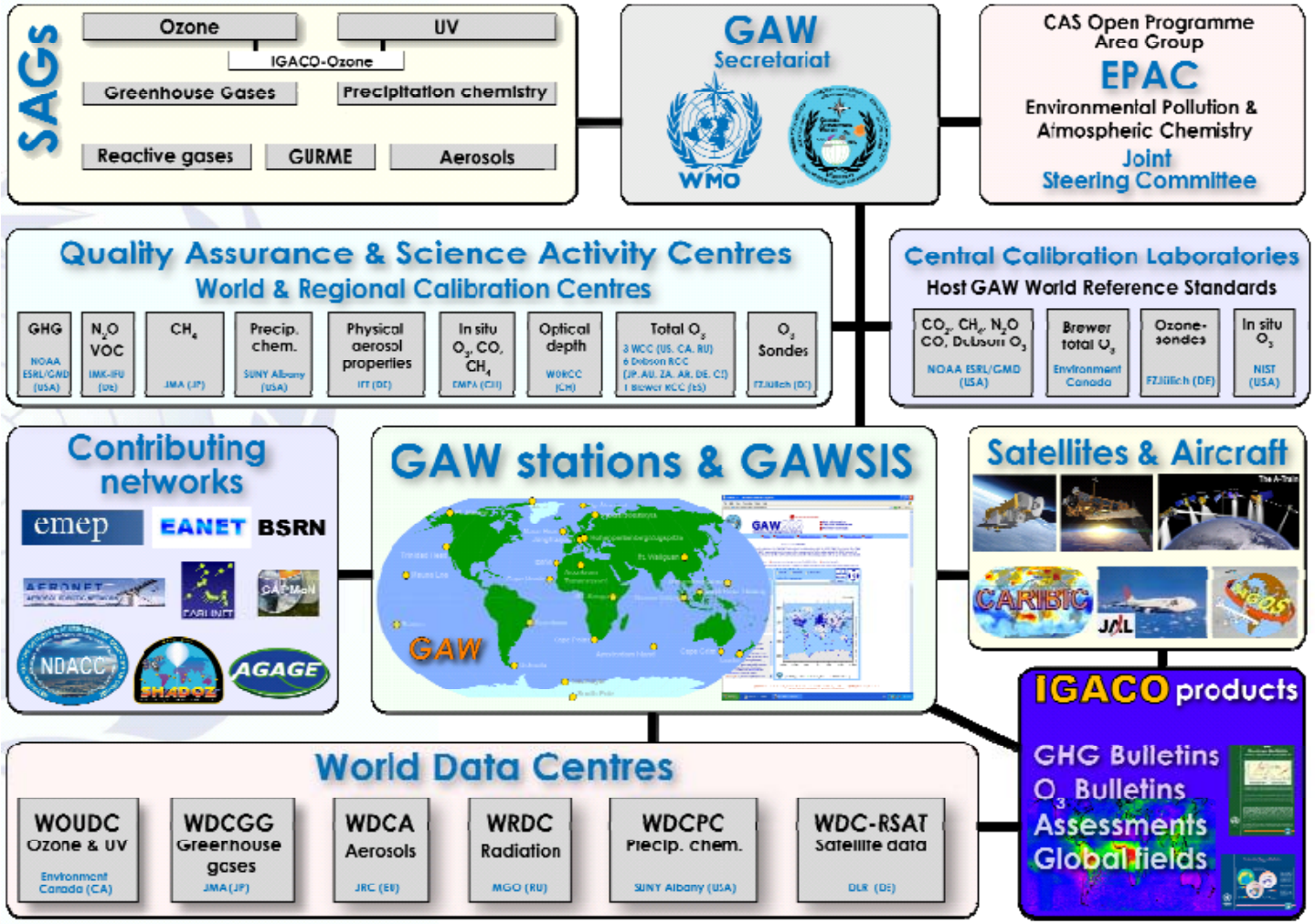
WMO Global Atmosphere Watch (GAW)

- Established in 1989 by merging long-term monitoring programmes dating back to the 1970s or earlier.
- Focuses on global networks for ozone, greenhouse/reactive gases, atmospheric wet deposition, UV radiation, and aerosols.
- Coordinates activities and data from hundreds of stations, including 26 Global Stations.



Structure of WMO/GAW

- GAW consists of national meteorological/hydrological services and other partners contributing to observing systems, experts groups and central facilities, and the secretariat.



WMO/GAW Central Facilities

- The following types of central facilities are operated by WMO Members and form the basis of quality assurance and data archiving for the GAW global monitoring networks.
  - Central Calibration Laboratory (CCL)
  - World Calibration Centre (WCC)
  - Quality Assurance/Science Activity Centre (QA/SAC)
  - World Data Centre (WDC)

Table 1: Overview of the GAW World Central Facilities (as of May 2007). The World Central Facilities have assumed global responsibilities, unless indicated (Am: Americas; E/A: Europe and Africa; A/O: Asia and the South-West Pacific).

Variable	QA/SAC	Central Calibration Laboratory (CCL) Host of Primary Standard	World Calibration Centre (WCC)	Regional Calibration Centre (RCC)	World Data Centre (WDC)
CO_2	JMA (A/O)	ESRL	ESRL		JMA
CH_4	Empa (Am, E/A) JMA (A/O)	ESRL	Empa (Am, E/A) JMA (A/O)		JMA
N_2O	UBA	ESRL	IMK-IFU		JMA
CFCs, HCFCs, HFCs					JMA

Source: WMO/GAW Strategic Plan: 2008–2015

Terms of Reference for CCLs

- Host in the long term (many decades) the GAW primary standard and scale for a particular variable.
- Serve the needs of the other quality assurance facilities and activities of GAW.
- Prepare or commission laboratory standards required by the GAW network members for calibration purposes.
- Supply well-calibrated air to GAW analytical laboratories as needed for conducting inter-comparisons (in collaboration with the World or Regional Calibration Centres).

Source: WMO/GAW Strategic Plan: 2008–2015

Data Quality Objectives (DQOs)

- **DQOs specify tolerable levels of uncertainty in the data, required completeness, comparability and representativeness based on the decision to be made.**

Source: WMO/GAW Strategic Plan: 2008–2015

Table 1. Recommended inter-laboratory (network) comparability of components discussed

Component	Inter-Laboratory comparability
CO_2	± 0.1 ppm (± 0.05 ppm in the southern hemisphere)
$\delta^{13}C\text{-}CO_2$	± 0.01 ‰
$\delta^{18}O\text{-}CO_2$	± 0.05 ‰
$\Delta^{14}C\text{-}CO_2$	± 1 ‰
O_2/N_2	± 1 per meg
CH_4	± 2 ppb
CO	± 2 ppb
N_2O	± 0.1 ppb
H_2	± 2 ppb
SF_6	± 0.02 ppt

Source: Report of the 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GAW Report No. 186)

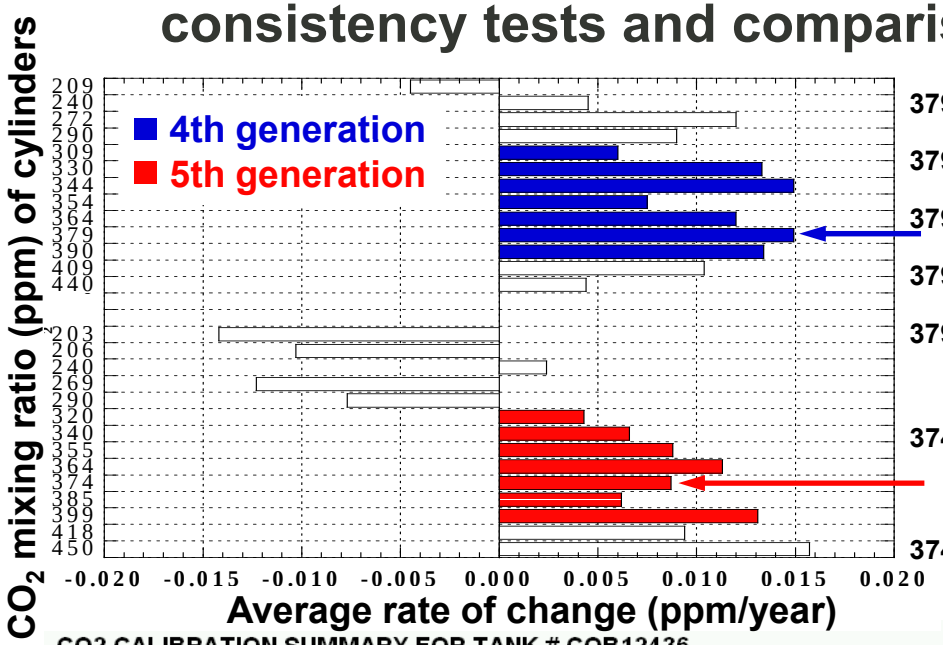
The WMO CO_2 Mole Fraction Scale

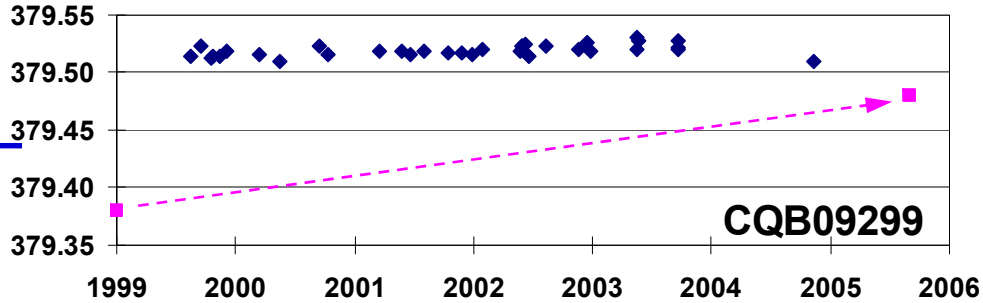
- In 1995, WMO designated NOAA/ESRL as the Central CO_2 Laboratory (CCL) responsible for the maintenance of the absolute WMO Mole Fraction Scale for CO_2. Before that time, the scale had been maintained by the Scripps Institution of Oceanography (SIO).
- In 1990, ESRL prepared 15 CO_2-in-air reference gas mixtures ranging 250–520 μmol mol^{-1}, calibrated at SIO by NDIR. The values assigned to the 15 primaries were based on both SIO NDIR measurements and ESRL manometric determinations between 1996 and 2001, and manometric determinations by ESRL alone starting in 2002.
- In September 2005, the WMO scale was revised, and a quadratic curve fit was used.
- In defining the revised scale for 2007 (WMO-X2007), the CCL chose to use a cubic polynomial for the curve fit.

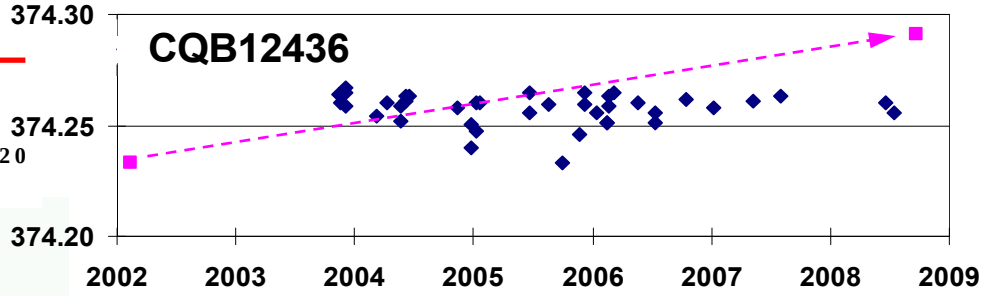
Source: GLOBALVIEW-CO2

Calibrations of JMA's CO_2 Standards at CCL

- Changes of ~ 0.01 ppm/year are seen in the mixing ratios of JMA's primary standards.
- They are larger than those estimated from the internal consistency tests and comparison with MRI's standards.







CO2 CALIBRATION SUMMARY FOR TANK # CQB12436

CO2 mixing ratios shown are on the WMO X2007 scale.

Filling Code A

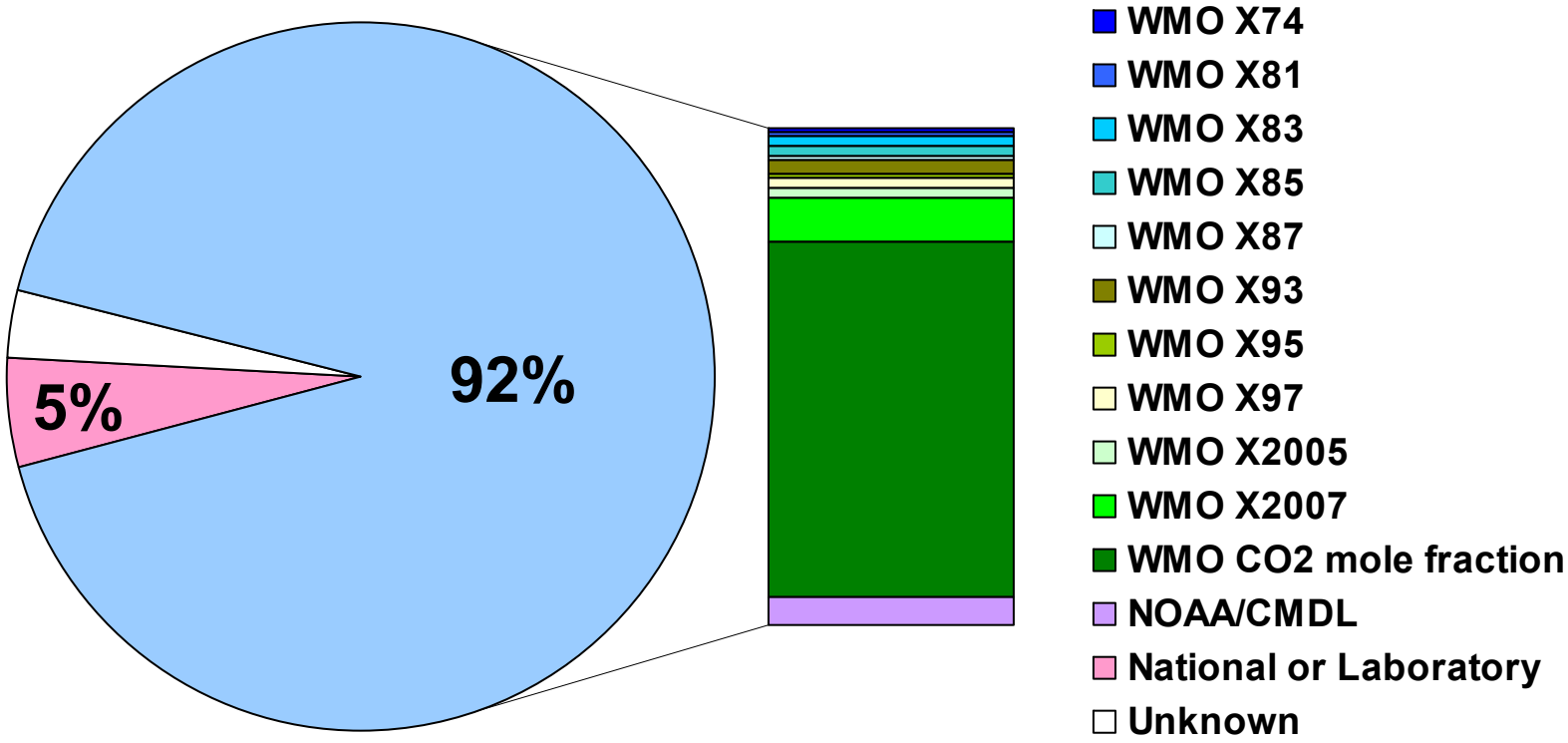
DATE	LOC	INST	PRESS	CONC.	S.D.	NUM	AVG	SDEV
2002-01-23	BLD	L9	2000	374.224	0.014	.		
2002-01-31	BLD	L9	2000	374.247	0.011	.		
2002-02-06	BLD	L9	2000	374.228	0.014	.		
2008-09-19	BLD	L9	700	374.283	0.010	.		
2008-09-24	BLD	L9	700	374.299	0.010	.		
						5	374.26	0.03

◆: Results of internal consistency tests

■: Re-assigned values on the X2007 scale

CO_2 Calibration Scales at the WDCGG

- More than 90% of the CO_2 data sets reported to the WDCGG are on the WMO or NOAA scale, but different scales exist.
- The WDCGG encourages contributors to submit data in latest WMO scales (WMO X2007 scale or whatever the latest scale is).



The WMO CH_4 Mole Fraction Scale

- The most current WMO scale of CH_4 is the NOAA04 scale.
- 16 mixtures of CH_4 in dry air were prepared using a gravimetric technique to define the new CH_4 standard scale covering the nominal range 300–2600 nmol mol^{-1}.
- CH_4 mole fractions in the new scale are a factor of (1.0124 ± 0.0007) greater than those expressed in the CMDL83 scale.
- Differences of 0.5 nmol mol^{-1}, 1.5 nmol mol^{-1} and ~ 6 nmol mol^{-1} are suggested with the scales of Tohoku University, Meteorological Research Institute (MRI) and Meteorological Service of Canada (MSC).

Reference: Dlugokencky, E. J., R. C. Myers, P. M. Lang, K. A. Masarie, A. M. Crotwell, K. W. Thoning, B. D. Hall, J. W. Elkins, and L. P. Steele (2005), Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.*, 110, D18306, doi:10.1029/2005JD006035.

CH_4 Calibration Scales at the WDCGG

Table 4. Status of the standard scales of CH_4 at laboratories with conversion factors.

Laboratory	WDCGG Filename Code	Calibration Scale	Conversion Factor
AEMET	IZO128N0000	NOAA/CMDL	1.0124
AGAGE	CGO540S0011,CGO540S0013,CMO445N0011, MHD653N0011,MHD653N0013,RPB413N0000, RPB413N0011,SMO514S0014,SMO514S0016, THD441N0000	Tohoku Univ.	1.0003
CESI	PRS645N0000	NOAA/CMDL	1.0124
CHMI	KOS649N0000	CHMI	0.9973
CSIRO	ALT482N0003,CFA519S0003,CGO540S0003, CYA766S0000,ESP449N0003,MAA767S0003, MLO519N0003,MQA554S0003,SIS660N0003, SPO789S0003	NOAA04	1
ENEA	LMP635N0000	NOAA/CMDL	1.0124
ENPA	JFJ646N0000	NOAA04	1
JMA	MNM224N0000,RYO239N0000,YON224N0000	NOAA04	1
KMA	AMY236N0000		
KSNU	ISK242N0000		
METRI	GSN233N0000		
MGO	TER669N0001	NOAA04	1
MRI	TKB236N0000	MRI	0.9973
NIES	COI243N0000,HAT224N0000	NIES	0.9973
NOAA/GMD	BRW471N0000,MLO519N0000, NOAA/GMD flask network*	NOAA04	1
	KPA432N0001,LEF445N0001,MCM777S0001 NZL543S0001,POC935S0001,SGI354S0001,SIO432N0001	NOAA/CMDL	1.0124
RIVM	KMW653N0000	NIST	0.9973
SAWS	CPT134S0000	NOAA04	1
UBA	DEU649N0000,NGL653N0000,SSL647N0000, ZGT654N0000,ZSF647N0010,ZUG647N0000	NOAA04	1

Source: WDCGG Data Summary, 2009

The WMO N_2O Mole Fraction Scale

- The most current WMO scale of N_2O is the NOAA-2006 scale.
- The NOAA-2006 N_2O calibration scale is based on gravimetrically prepared compressed gas standards and defined by 13 standards with dry air mole fractions ranging from 262–371 nmol mol^{-1}.
- The new scale (NOAA-2006) is 0.059% lower than the NOAA-2000 scale at 320 ppb.
- The NOAA-2006 scale is, on average, 0.23% higher than that defined by NIST Standard Reference Materials 2608 and 2609, and an average of 0.01% lower than the Scripps Institution of Oceanography SIO-98 scale over the range 298–319 ppb.

Reference: Hall, B. D., G. S. Dutton, and J. W. Elkins (2007), The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954.

N_2O Calibration Scales at WDCGG

Table 5. Status of the standard scales of N_2O at laboratories.

Submitter	WDCGG Filename Code	Calibration Scale	Conversion Factor
AGAGE	ADR652N0010,CGO540S0011,CGO540S0012, CGO540S0013,CMO445N0010,CMO445N0011, MHD653N0011,MHD653N00013,RPB413N0000, RPB413N0010,RPB413N0011,SMO514S0014, SMO514S0015,SMO514S0016,THD441N0000	SIO 1998	1
CSIRO	ALT482N0003,CFA519S0003,CGO540S0003, CYA766S0000,EPC449N0003,MAA767S0003, MLO519N0003,MQA554S0003,SIS660N0003, SPO789S0003	CSIRO	0.9983
ENEA	LMP635N0001	CMDL 2000	0.999402
EMPA	JFJ646N0000	SIO 1998	1
GERC	GSN233N0103		
JMA	RYO239N0000	NOAA-2006	1
KMA	AMY236N0000		
METRI	GSN233N0000		
MRI	MMB243N0000	MRI	
Nagoya University	NGY235N0000		
NIES	HAT224N0000	NIES	
NILU	ZEP678N0000		
NOAA/GMD	ALT482N0001,BRW471N0001,BRW471N0011, CGO540S0001,KUM519N0001,MLO519N0001, MLO519N0011,NWR440N0001, NWR440N0011, SMO514S0001, SMO514S0011,SPO789S0001, SPO789S0011	CMDL 2000	0.999402
	BRW471N0010, MLO519N0010, NWR440N0010, SMO514S0010, SPO789S0010,SUM672N0000	NOAA-2006	1
SAWS	CPT134S0000	CMDL 2000	0.999402
UBA	SSL647N0000,ZSF647N0010	SIO 1998	1

Source: WDCGG Data Summary, 2009

Interlaboratory Comparison Exercises

- **If possible scales should be compared directly, else use ICP information for adjustments for interpretative studies only. Measurements should not be corrected based on ICPs.**

Source: Minutes from the Meeting of the WMO Scientific Advisory Group for Greenhouse Gases, 11 September 2009, Jena, Germany

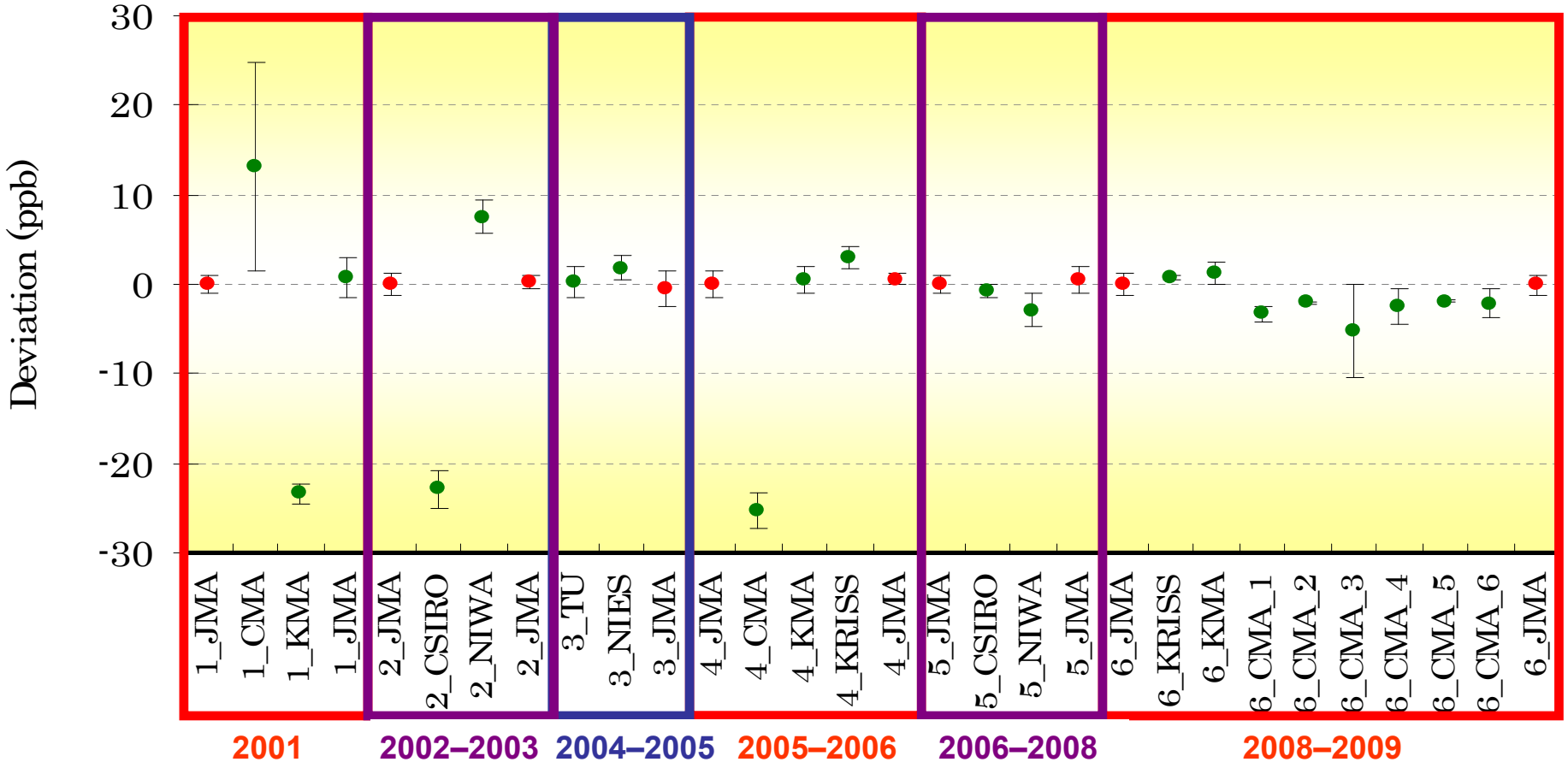
Table 2. 2002 - 2007 WMO Round-Robin Intercalibration Results
Carbon Dioxide Concentrations (Preliminary).

Laboratories	Analysis Date	Report Date	TANK # CO_2, µmol mol^{-1}			Differences (Lab minus NOAA) CO_2, µmol mol^{-1}			Description of reported standard scale
GROUP ONE (Tank #4532, #4409, #4584)			4532	4409	4584	4532	4409	4584	
US – NOAA average			354.91	368.14	384.81				
JP - Tohoku U.	Jan.2003	Mar.2004	354.80	367.95	384.52	-0.11	-0.19	-0.29	Gravimetric, Tohoku U. 2003 scale
JP – NIES	Apr.2003	Mar.2004	354.81	367.99	384.67	-0.10	-0.15	-0.14	Gravimetric, NIES95 scale
JP – MRI	July.2003	Mar.2004	354.75	367.98	384.73	-0.16	-0.16	-0.08	Gravimetric, MRI 1987 scale
JP – AIST	Sept./Dec.2003	Mar.2004	354.80	367.92	384.52	-0.11	-0.22	-0.29	Gravimetric, Tohoku U. 2003 scale
JP – JMA	Jan.2004	Mar.2004	355.04	368.14	384.79	0.13	0.00	-0.02	WMO X2005 scale
Korea – KMA (KGAWO)	Mar./Jun.2004	July.2004	354.47	368.02	384.73	-0.44	-0.12	-0.08	4 tanks NOAA and 2 tanks KRISS
CN - CMA (WLG)	July.2004	Nov.2004	354.86	367.95	384.71	-0.05	-0.19	-0.10	WMO X2007 scale
CN - CMA (BJ)	Aug.2004	Nov.2004	354.88	367.94	384.83	-0.03	-0.20	0.02	WMO X2007 scale
US – SCRIPPS (CMM)	June.2005	June.2006	355.14	368.31	385.01	0.23	0.17	0.20	Manometric, CMM
US - SCRIPPS (ECM II)			355.01	368.16	384.83	0.10	0.02	0.02	Manometric, ECM II
FR – LSCE	Oct./Nov.2005	Dec.2005	354.86	368.03	384.72	-0.05	-0.11	-0.09	Calibrated by NOAA between 2001 and 2002

Source: Report of the 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GAW Report No. 186)

CH_4 Intercomparisons

- **JMA, as an activity of the WMO/GAW World Calibration Centre for CH_4 in Asia and the South-West Pacific, organizes intercomparisons for CH_4 among laboratories in Asia and the South-West Pacific.**



The WMO-CIPM Agreement (2002)

- **WMO and the International Committee for Weights and Measures (CIPM) will consult together to ensure that data, related in particular to measurements of state and composition of atmosphere and water resources, coming from the programmes organized under the auspices of WMO are properly based on units traceable to the SI through the procedures of the Mutual Recognition Arrangement (MRA) for National Measurement Standards drawn up by CIPM and those of the Technical Regulations of the Organization.**

AGREEMENT BETWEEN THE WORLD METEOROLOGICAL ORGANIZATION AND THE INTERNATIONAL COMMITTEE FOR WEIGHTS AND MEASURES

Text approved by the CIPM on 10 October 2001

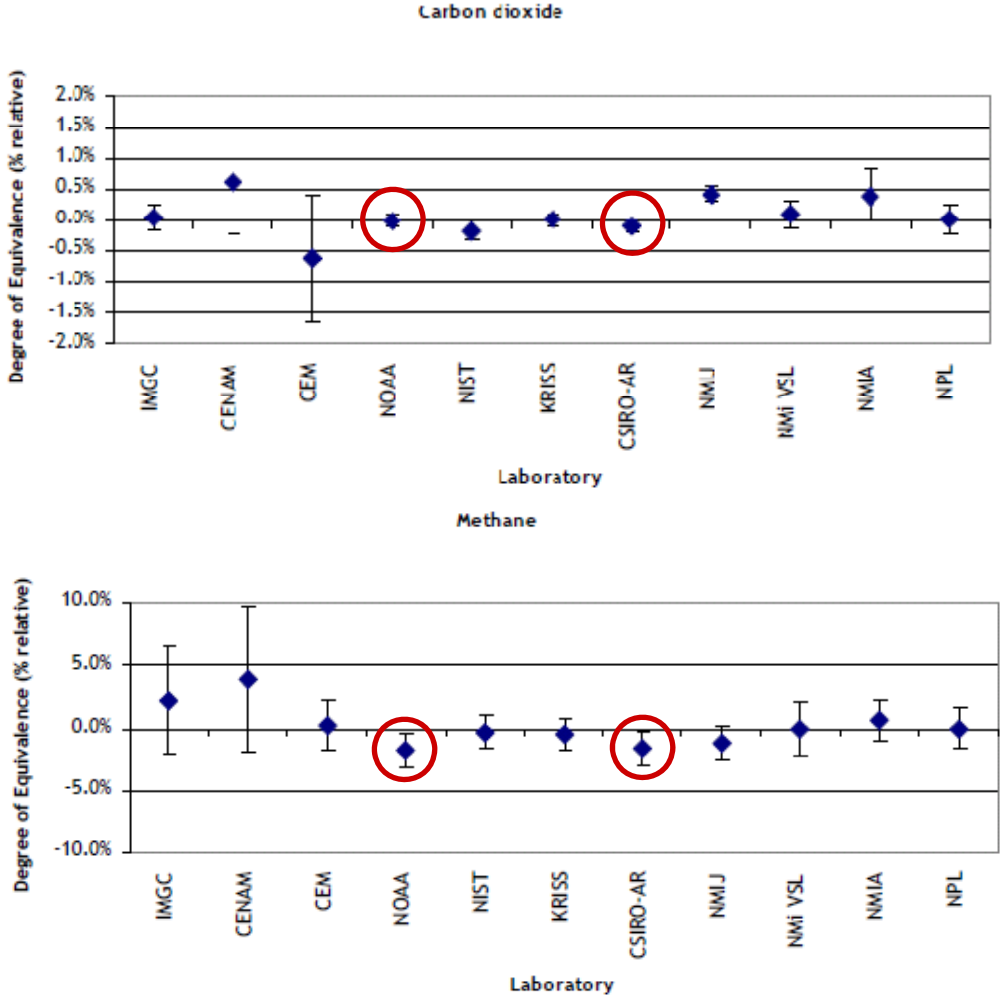
ARTICLE I

Cooperation and collaboration

1. The World Meteorological Organization (WMO), referred hereinafer as "the Organization", and the International Committee for Weights and Measures, referred hereinafter as "the Committee", agree that with a view to facilitating the implementation of their objectives, set respectively in the Convention of WMO, and in the Metre Convention, they will act in close cooperation with each other and consult each other regularly in regard to matters of common interest.

International comparison CCQM-P41

- **In 2003, a comparison CCQM-P41 was carried out between NMIs and WMO laboratories for greenhouse gases.**



Source: Adriaan M. H. van der Veen et al., 2007, Metrologia 44

WMO-CIPM Mutual Recognition Agreement

- WMO plans to sign a Mutual Recognition Agreement (MRA) with the CIPM.
- In general, the MRA assures equivalency among standards among its signatories through “key comparisons”.
- WMO/GAW will still recommend that GAW participants maintain a direct link to the CCLs for GHG standards.
- Once signed, CCLs will need ISO certification. They will need to prepare quality systems (QS) that meet requirements of ISO guidelines 17025 and 34.
- NIST will help NOAA with this process; the QS must then be approved by the SIM (InterAmerican Metrology System), and it must demonstrate traceability to SI standards.
- There will be a meeting on this issue between WMO and BIPM in Geneva, 30 March – 1 April 2010.

Source: Minutes from the Meeting of the WMO Scientific Advisory Group for Greenhouse Gases, 11 September 2009, Jena, Germany

Summary

- WMO Mole Fraction Scales have been established for CO_2, CH_4, N_2O and CO. A WMO scale for SF_6 is to be established, but WMO scales for CFCs have yet to be agreed upon.
- The WMO scales and some other scales are interconvertible through conversion factors established from comparisons among different laboratories.
- International comparisons are organized to determine the precision of the current practice of international calibrations, not to distribute calibration scales.
- WMO and the International Committee for Weights and Measures (CIPM) reached an agreement in 2002 to cooperate with and consult each other. WMO plans to sign a Mutual Recognition Agreement (MRA) with the CIPM.