Better Standards, Better Life!

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Standards for Greenhouse gas Monitoring

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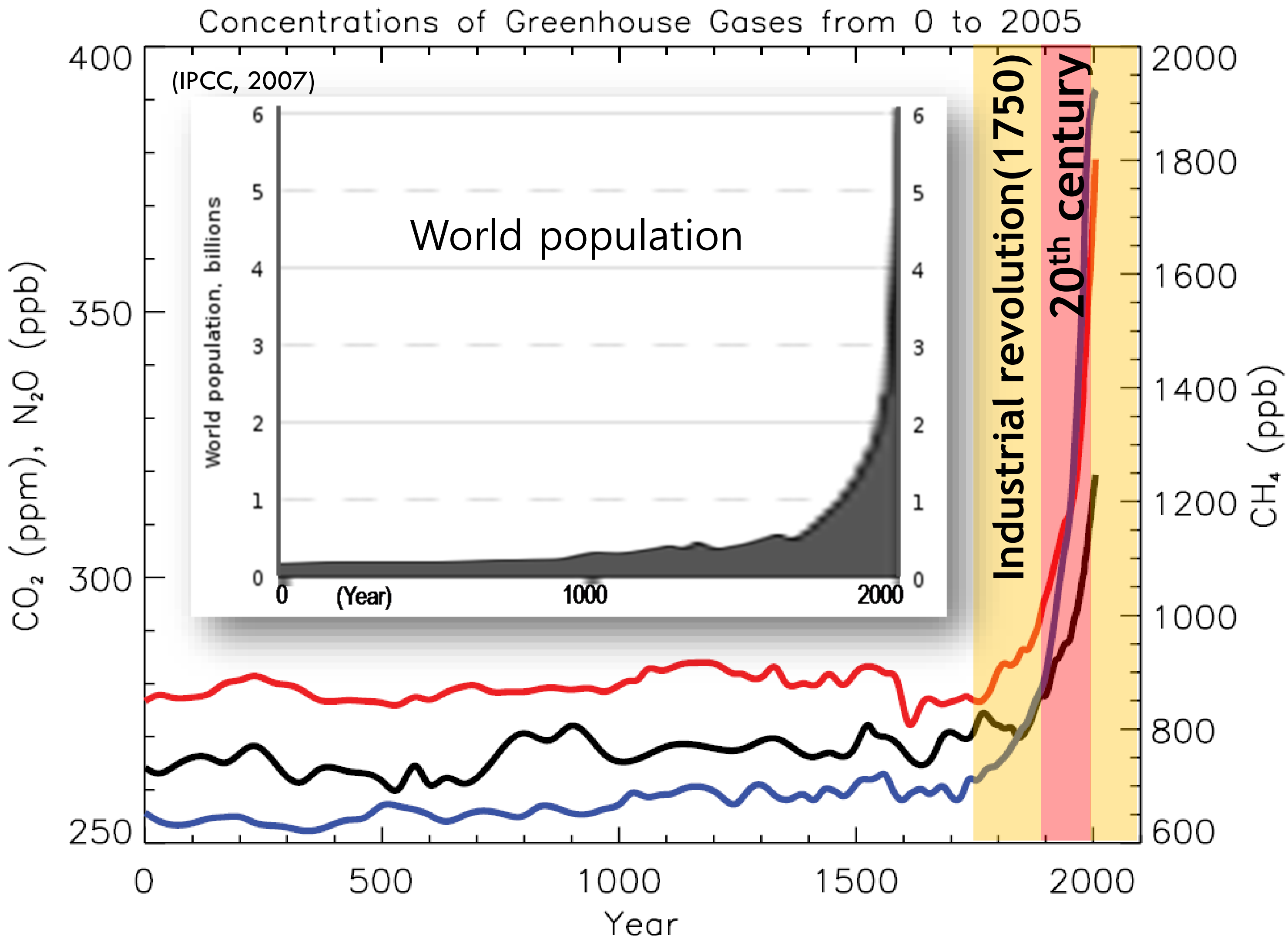
Greenhouse Gases Concentration



First step for the Climate Change Science

- To better understand the physical, chemical, biological and geological processes and the interactions that governs the climate system
  - More accurate and continuous real time observation
    - Spatial scales: global to local
    - Temporal scales: weeks to millions of years
  - To collect data as evidences and predict CC

MRA between WMO and BIPM

On April 2010

Measurement Challenges in Global Observation Systems for Climate Change Monitoring: *Traceability, Stability and Uncertainty*

- Three institutes designated by the WMO can now participate fully in the MRA
- A new set of opportunities for collaboration and for the NMIs to support global atmospheric monitoring

Cooperation between WMO & BIPM

- Greenhouse Gases effect to Global Warming and should be monitored
- Global Atmosphere Watch Program needs precise and stable standard reference gas mixtures
- WMO designates Central Calibration Lab (CCL) for developing accurate and precise references. CCL participates the key comparison program.
- NMIs establish Primary methods for accurate measurement and support CCLs

WMO GAW QA system

- According to the WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 -2015 (GAW report 172) WMO-GAW have paid attention to systematically improve quality of data observed at the global or regional monitoring site.
- To produce good measurement data, it is essential to ensure traceability over the world as well as to establish a controlled quality system.
- For the implementation of Quality system recommended by GAW program
  - Detect small trends (through DQO)
  - Detect small spatial gradients
  - Ensure long-term stability of observations
  - Data comparability (on the same scale)

WMO primary standards (CO_2)

- Preparation:
  - Manometric technique for CO_2, Established in CCL (NOAA), Unc.(1σ): ~ 0.07 ppm*
  - Now, Gravimetric Method; CH_4, N_2O, CFC, PFC

* **Zhao, C. L.** and **P. P. Tans**, (2006), Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air,

- Dissemination
  - Transfer Standard: Air or Modified Air
  - NDIR Calibration with Manometric Value by (1σ): 0.02 ppm for CO_2

Primary Reference Material

- Purity assessment
  - Molecular weights of source gases (isotopic ratio)
  - Impurity analysis based on final concentration
- Accurate mixing (Gravimetry)
- Internal consistency by comparison (one set at a time)
- Stability test (6 months for short term)
- Verification through KC (including uncertainty)
- Register to BIPM CMC (as NMI)
- Validation of life time by periodical reproduction
- Expensive ? support industry & government (by national body)

KRISS activity on GG monitoring

- International cooperation bet. BIPM and WMO
- International comparisons
  - Global average of CO_2, CH_4, N_2O, SF_6, CFCs, HFCs
  - International comparison results

- KMA and KRISS cooperation
  - Mutual cooperation since 1998
  - Continuous greenhouse monitoring at Anmyeon & Ulleung in Korea
  - Air achieve and halocarbon measurement

Traceability and Harmonization

Key Comparisons for the demonstration of equivalency between NMI's in their analytical capability to certify the composition of gas mixtures (analytical comparison) and their capability to prepare SI-traceable gas measurement standards (preparative comparison)

International Comparison

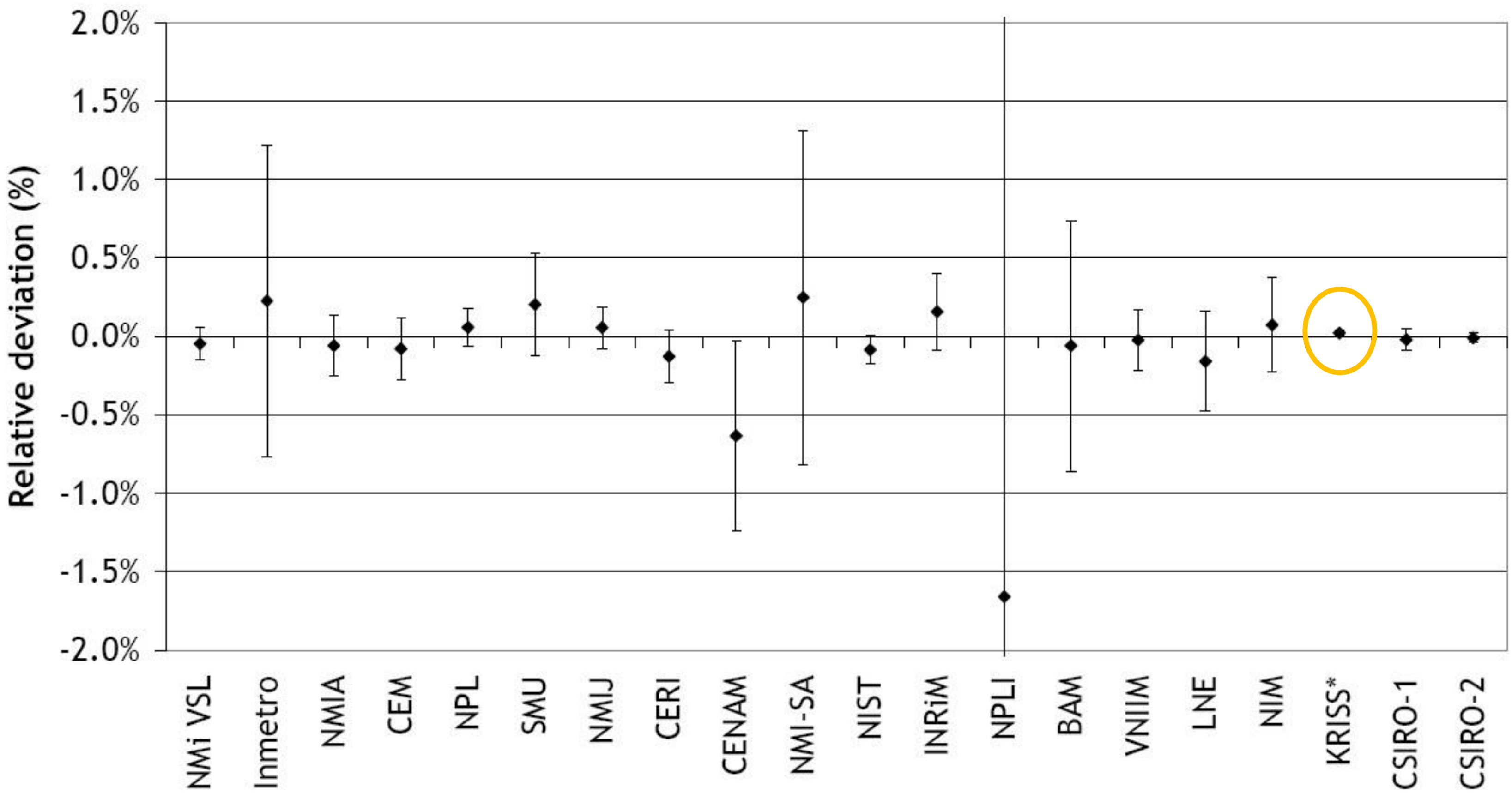
- International comparison activity
  - coordination : BIPM – CCQM
  - BIPM (Bureau international des Weight and measures)
  - CCQM (Consultative Committee for Amount of Substance)
    Metrology in Chemistry, Working group (NMI)
  - Regional activity: APMP/TCQM
- Quality system : Peer Reviewed by 5 years
  - management, technology
  - registration of BIPM CMC List : KRISS CRM # 130 (2005)
  - Service (measurement capability)

CCQM Key Comparisons

- 2002 CCQM-P41 Greenhouse gases
- 2004 CCQM K15 CF4 and SF6 emission level(coordination by KRISS)
- 2005 CCQM K51 CO in nitrogen (5 μmol/mol)
- 2007 CCQM K52 CO2 ambient level
- 2009 CCQM K68 N2O in artificial air, ambient level(coordination by KRISS)
- 2012 CCQM K82 CH4, ambient level
- 2012 CCQM K83 CFCs and HFCs, ambient level (+ EMPA, SIO)
- 2012 CCQM K84 CO in air, ambient level(coordination by KRISS)

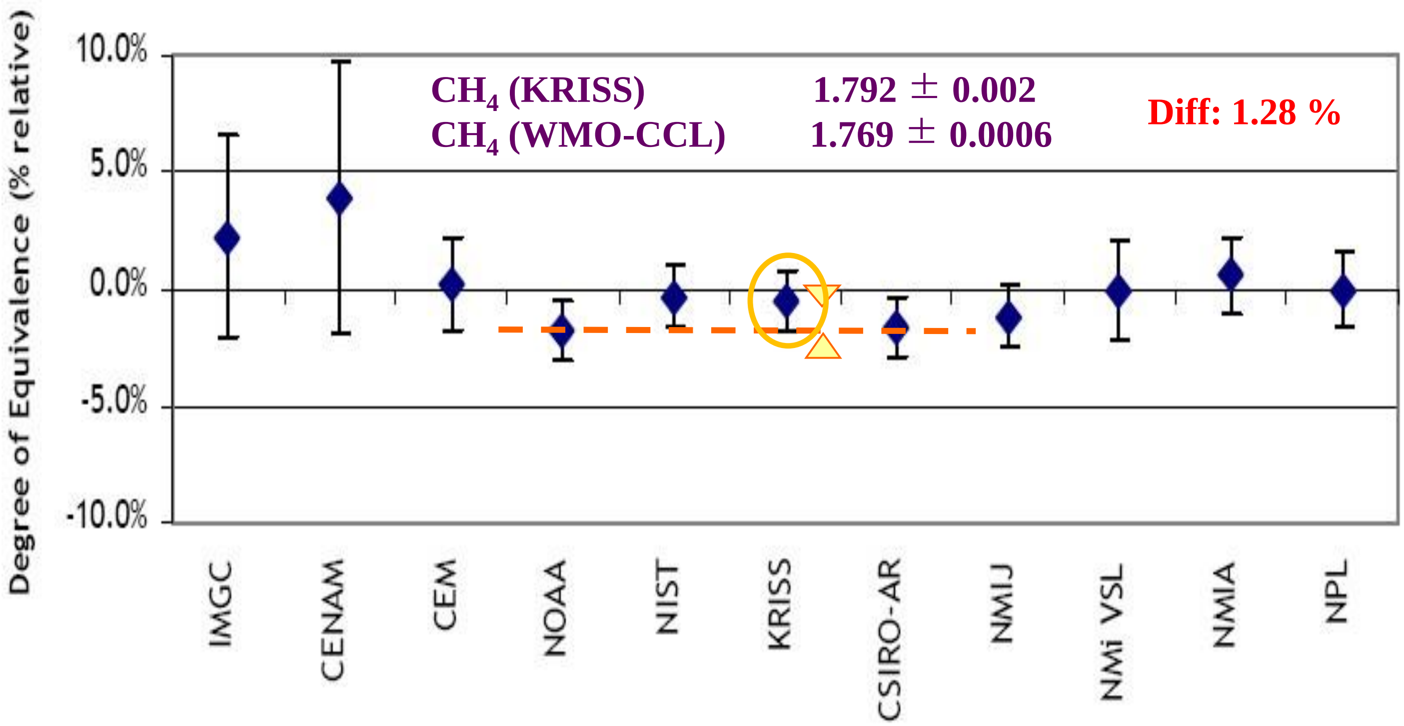
International comparison (CCQM-K52, 2008)

- Coordinating Lab: VSL (Netherland)
- Substance: Carbon dioxide in Synthetic Air



International comparison (CCQM-P41, 2003)

- **Coordinating Lab: NMi-VSL (Netherland)**
- **Substance: CH_4 in Synthetic Air**

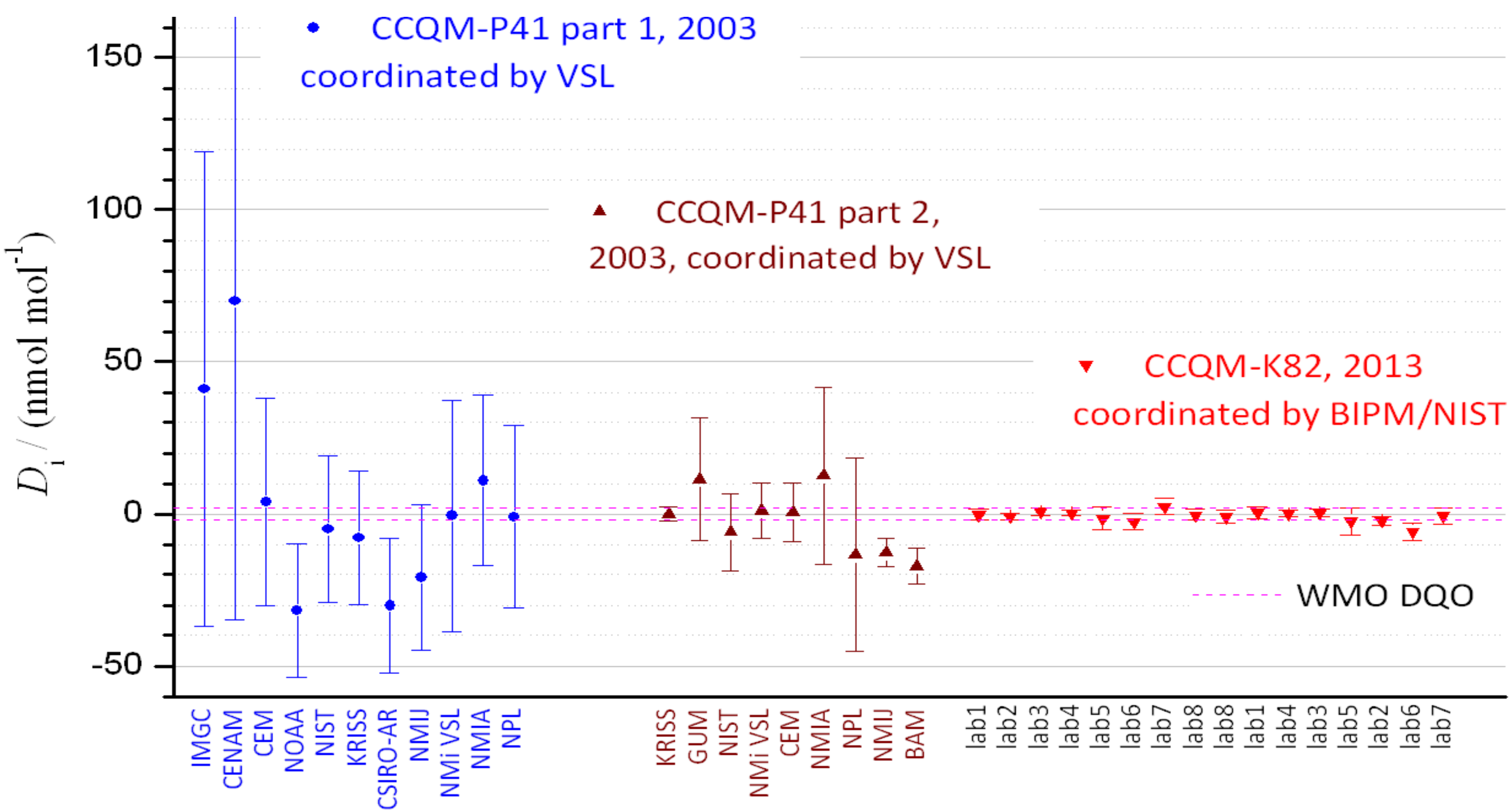


Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale (1.24 % higher than before)

：Dlugokencky, E. J. et. al., **(2005)**, *JGR-Atmospheres, 110*

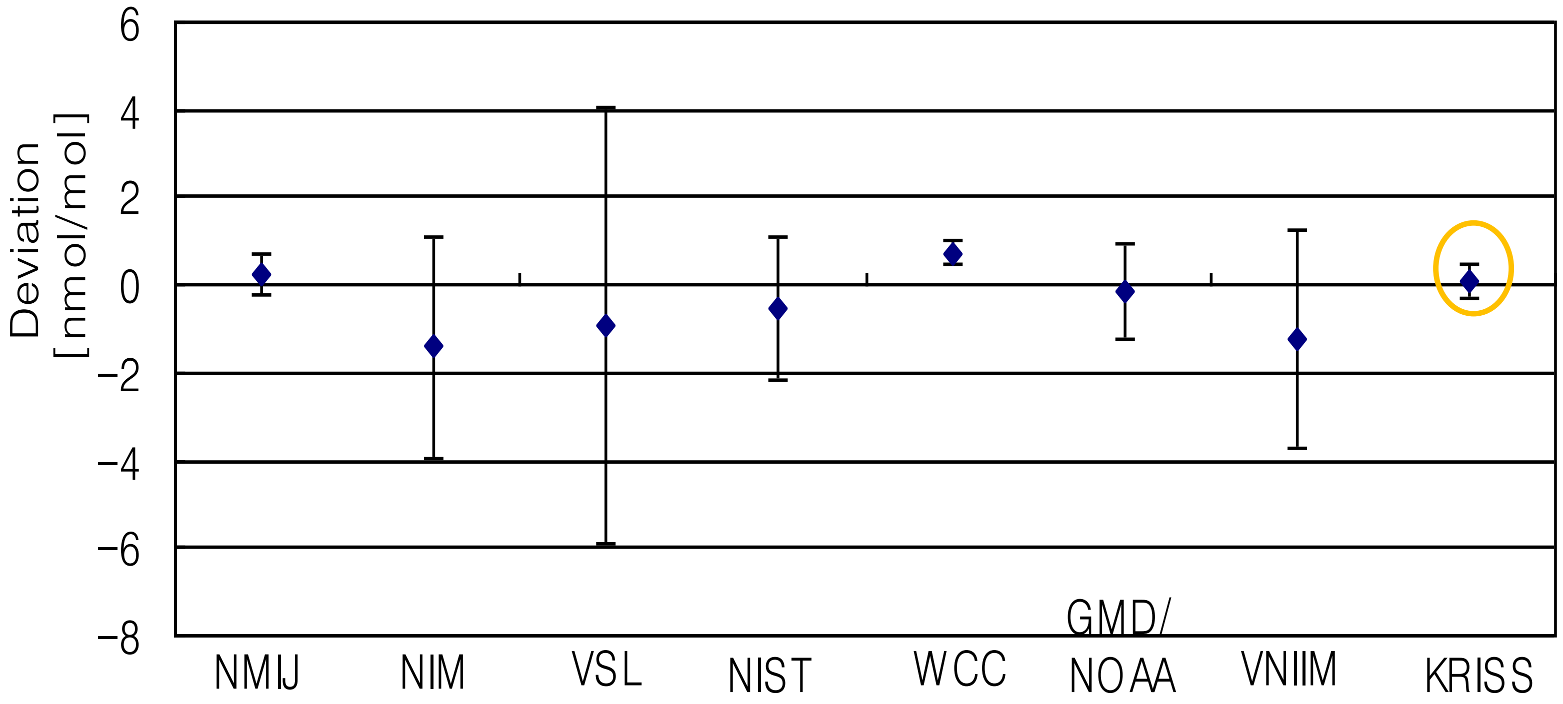
International comparison (CCQM-K82, 2014)

- Coordinating Lab: BIPM, 2014
- Substance: CH_4 in Synthetic Air



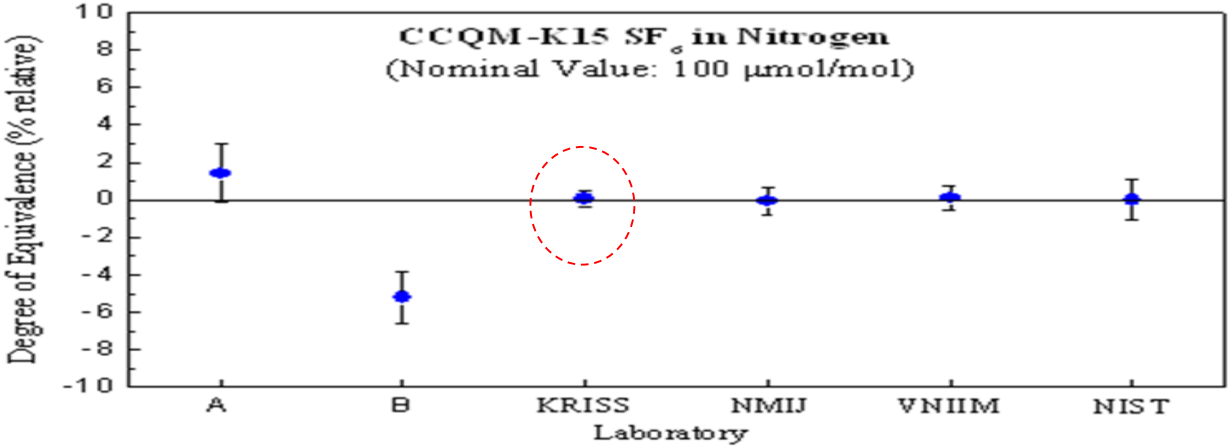
International comparison (CCQM-K68, 2010)

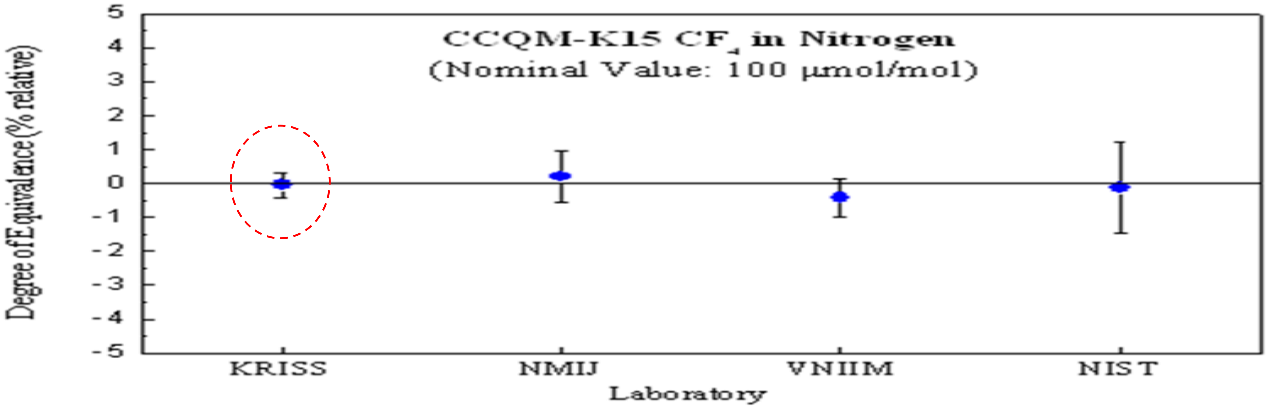
- Coordinating Lab: KRISS
- Substance: Nitrous oxide 320 nmol/mol in Synthetic Air



International comparison (CCQM-K15, 2003)

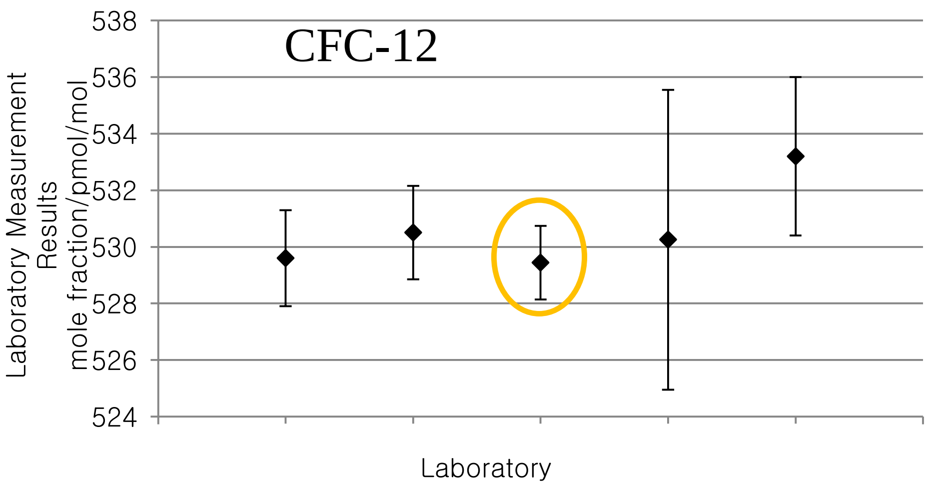
- Coordinating Lab: KRISS
- Substance: SF_6 & CF_4 hundred μmol/mol level

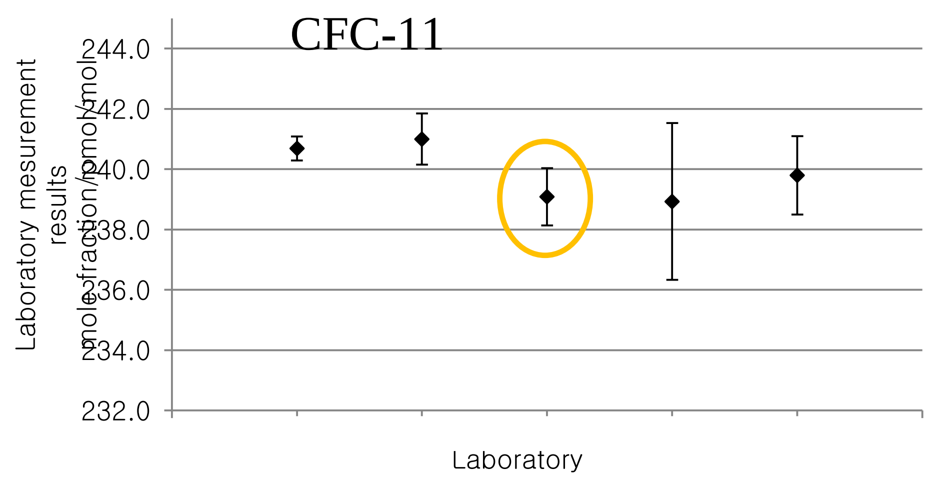


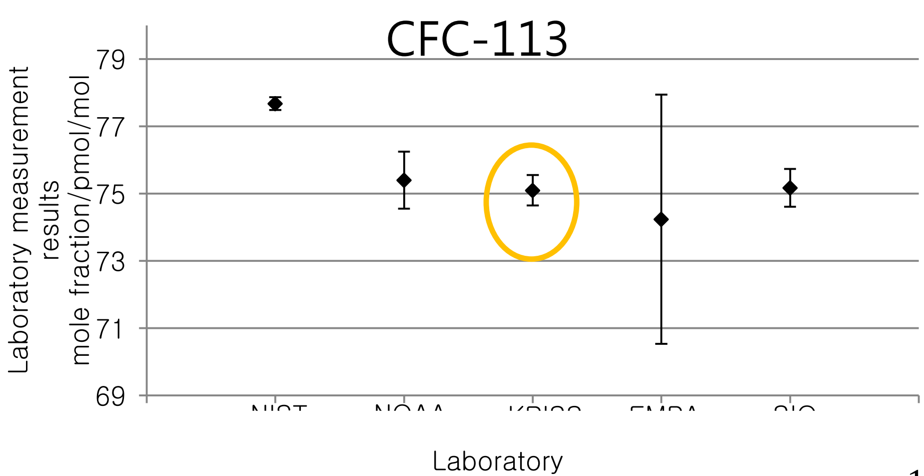


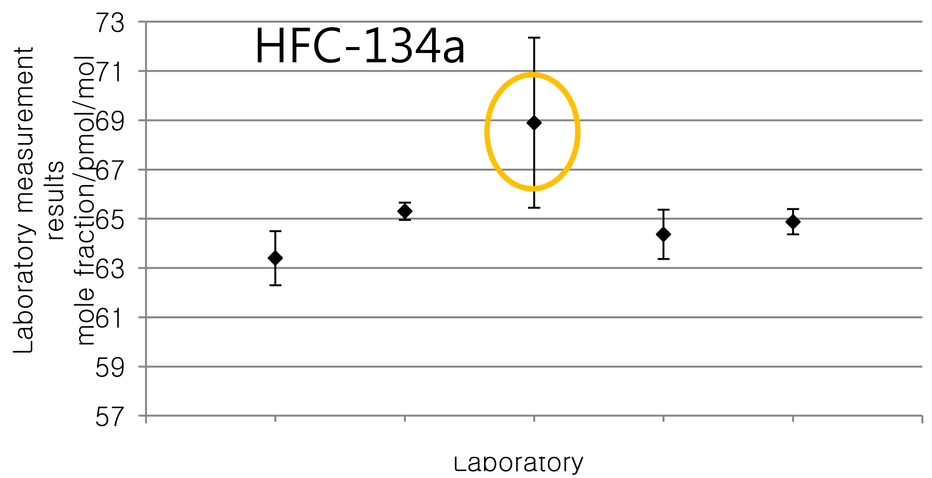
International comparison (CCQM-K83, 2013)

- Coordinating Lab: NIST
- Substance: ambient level Halocarbons in real air



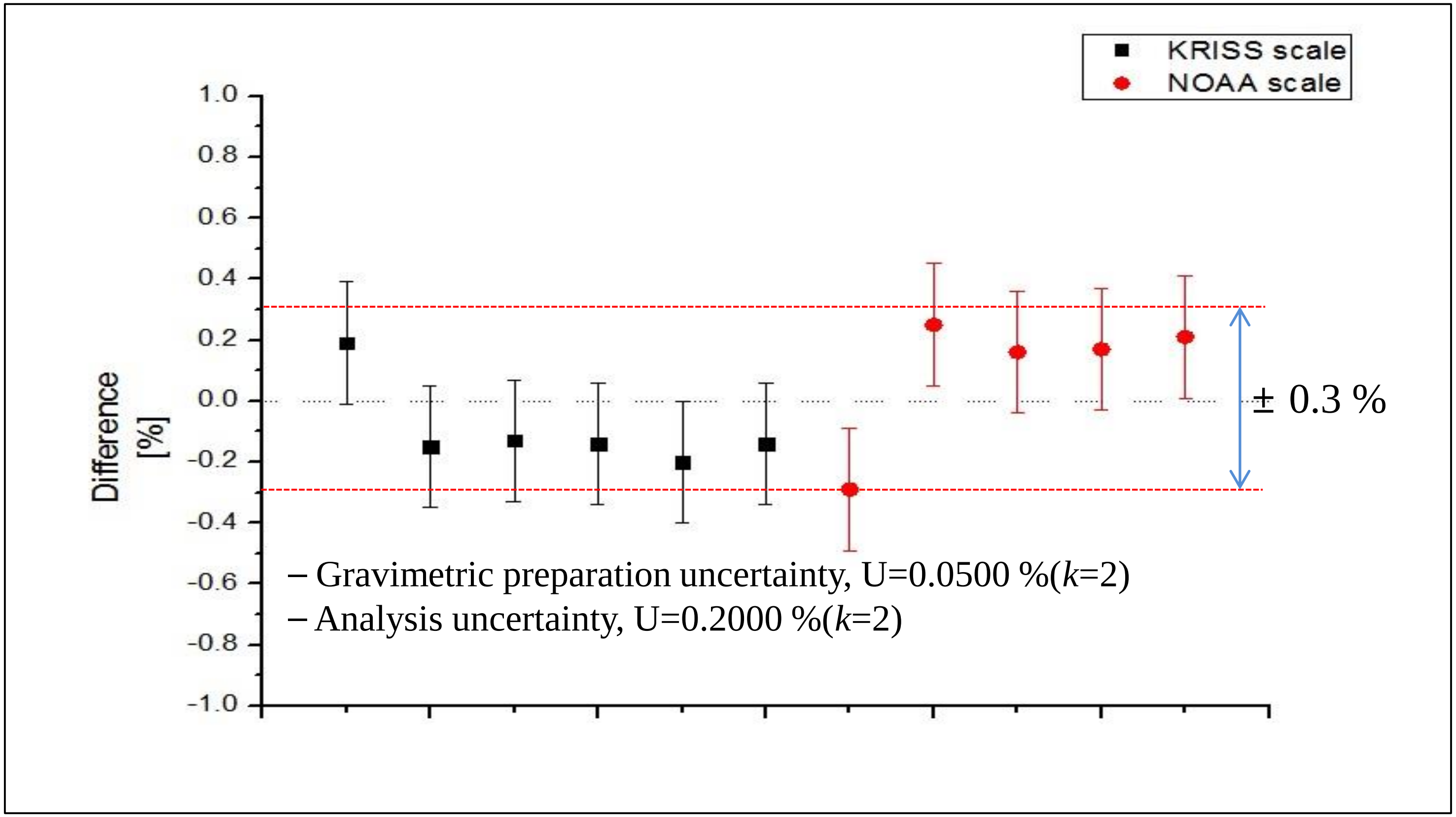






Bilateral comparison (NOAA & KRISS, 2014)

- **Coordinating Lab: KRISS**
- **Substance: SF_6 ambient level in air**



- As a result of the comparison, NOAA scale was updated to a new 2014 scale.

Standard reference gas mixtures

Standard reference gas mixtures

substance	Preparation method	Impurity analysis	Range of Certified Values in Reference Materials	Uncertainty (k=2) [U=2*u=2*]	Dissemination	Validity period /cylinder	ref
CO_2	Gravimetry/ 3 step	CO_2, N_2, O_2, Ar	above 10 μmol/mol	0.06 at 380 μmol/mol	Air /Air modified	2 year/Al*, 29.5L	CCQM-K3, 52 CCQM-K120
CH_4	Gravimetry/ 4 step	CH_4, N_2, O_2, Ar	above 100 nmol/mol	0.0005 at 1.9 μmol/mol	Air /Air modified	2 year/Al*, 29.5L	CCQM-P41, K82
N_2O CO	Gravimetry/ 5 step	N_2O, N_2, O_2	above 50 nmol/mol above 100 nmol/mol	0.2 at 320 nmol/mol 1.0 at 350 nmol/mol	Air /Air modified	2 year/Al*, 29.5L	CCQM-K68 CCQM-K84
SF_6 NF_3	Gravimetry/ 6 step Gravimetry/ 6 step	SF_6, N_2, O_2 NF_3, N_2, O_2	above 6 pmol/mol for SF_6 above 1 nmol/mol for NF_3	0.04 at 6 pmol/mol SF_6 0.01 at 1 nmol/mol NF_3	Air /Air modified	2 year/Al*, 29.5L	CCQM-K15, Paper preparation
PFCs	Gravimetry/ 6 step	CF_4 (C_2F_6), N_2, O_2	above 10 pmol/mol for CF_4 above 100 μmol/mol for C_2F_6	0.5 at 100 pmol/mol CF_4	Air /Air modified	2 year/Al*, 29.5L	CCQM-K15
HFCs	Gravimetry	HFC23, N_2, O_2	above 30 pmol/mol for HFC23	2 at 100 pmol/mol for HFC	Air /Air modified	2 year/Al*, 29.5L	CCQM-K83
CFCs HCFCs	Gravimetry/ 4~5 step	CFC 11,12,113, N_2, O_2	μmol/mol~50 pmol/mol for CFC 11,12,113	0.5 at 100 pmol/mol for CFC	Air /Air modified	2 year/Al*, 29.5L	CCQM-K83

➢ traceable to SI, uncertainty level with in WMO recommendation, Al*: Al Barrel polished (Luxfer or Catrina), ★ Additionally δ13C/CO_2, δ13C/CH_4,

Ongoing research on GG measurement

- Isotope analysis and isotope ratio analysis
- Remote measurement of atmospheric species
  - Ground remote observation for tracking source and sink
  - Global networking on carbon observation
- Aerosol measurement
- Emission measurement
  - Energy
  - Agriculture
  - Industry emission

Closing remark

- Significant contributions have been made by several NMIs to the standards used to underpin the evidence base for global GG monitoring.
- International collaboration is essential to monitor and predict CC and will greatly increase leverage in the future
  - WMO "Global Atmosphere Watch", now part of the CIPM-MRA
  - Global networking on GG observation
- Future challenges will be
  - Greater focus on standards in real matrices ("whole air")
  - Understanding of data (and uncertainties) in a way that is compatible with scales with long-term stability and accuracy