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EMPA
Materials Science & Technology

World Calibration Centre for Carbon Dioxide (Audits) –
Supporting the Quality of the Global Observation System

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GAW WCC-Empa
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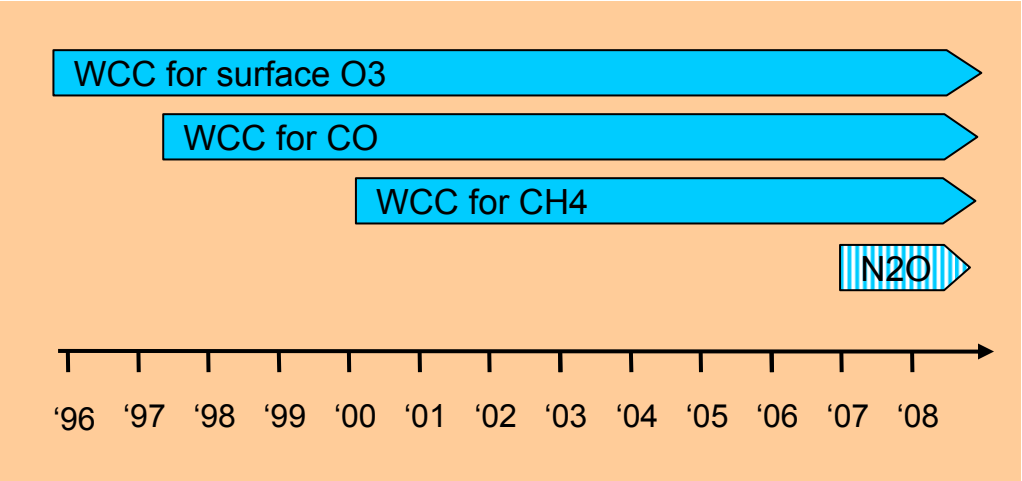
Outline

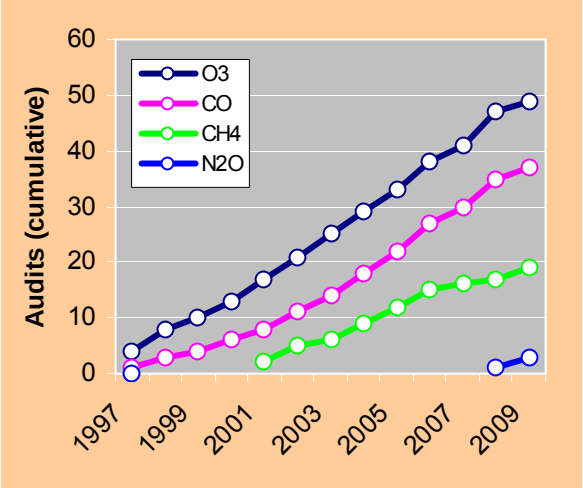
- History and mandate of WCC-CO_2 (Audits)
- System and performance audits
- Traceability of WCC-CO_2 to CCL
- Transfer of the WMO scale to travelling standards
- Evaluation of inter-comparison data
- Conclusions

History of WCC-Empa

- World Calibration Center for Surface Ozone, Carbon Monoxide and Methane
  - established 1995, 1 full-time staff
  - Surface Ozone 1996
  - Carbon Monoxide 1997
  - Methane 2000
  - Nitrous Oxide 2007 (collaboration with WCC-N2O)

See P2, Zellweger et al.

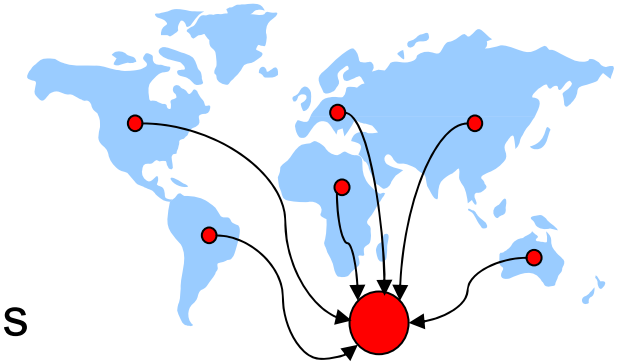




WCC-Empa

- Scope
  - Surface ozone, carbon monoxide,
  - Methane, (nitrous oxide), carbon dioxide (from 2010)

- Primary Tasks
  - Ensure traceability of measurements at Global GAW stations to designated GAW Reference Standard
  - Support stations with regards to instrument and/or measurement problems
  - Capacity Building, "1:1"-Training



Towards a WCC-CO_2 (Audits)

- 2001-2008 — Stations audited by WCC-Empa have repeatedly requested that CO_2 be included
- Feb 2009 — Funding secured from MeteoSwiss with in-kind contributons from Empa to expand the scope of WCC-Empa
- March 2009 — Formal proposal for establishment of WCC-CO_2 (Audits) is submitted to WMO and SAG GG
- April 2009 — Proposal reviewed by SAG GG; recommendation is made to JSC OPAG-EPAG
- May 2009 — JSC OPAG-EPAC approves proposal; designates Empa as the WCC-CO_2 (Audits)
- June 2009 — Practical preparations commence

Mandate of WCC-CO_2 (Audits)

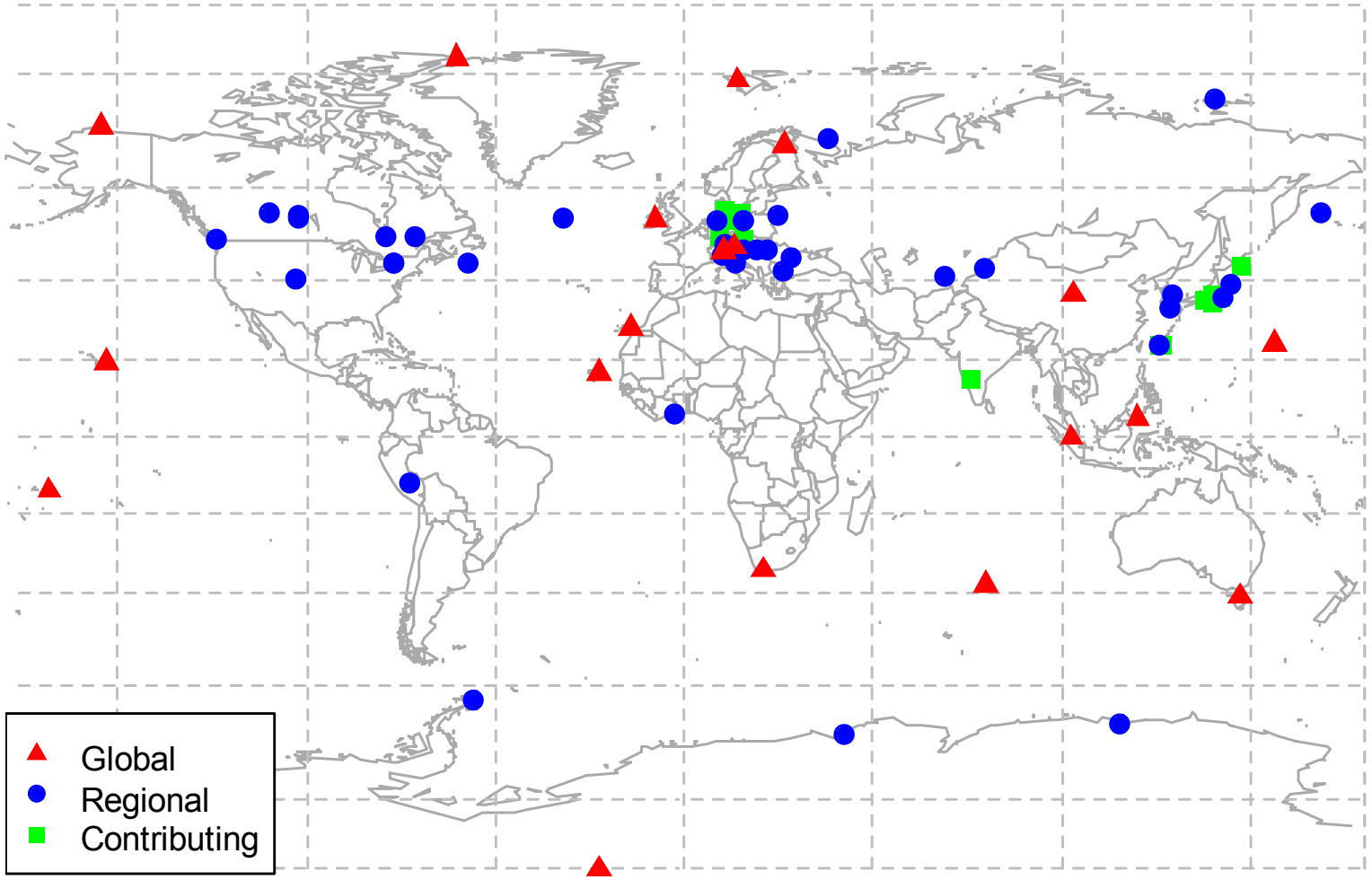
WCC-CO_2 (Audits) performs system and performance audits of continuous CO_2 measurements at Global GAW stations world-wide.

A **system audit** is a check of the overall conformity of a station with the principles of the GAW QA system. It involves an assessment of station siting, infrastructure, organization, operation, etc. The reference for conformity of a station will evolve as the GAW QA system evolves.

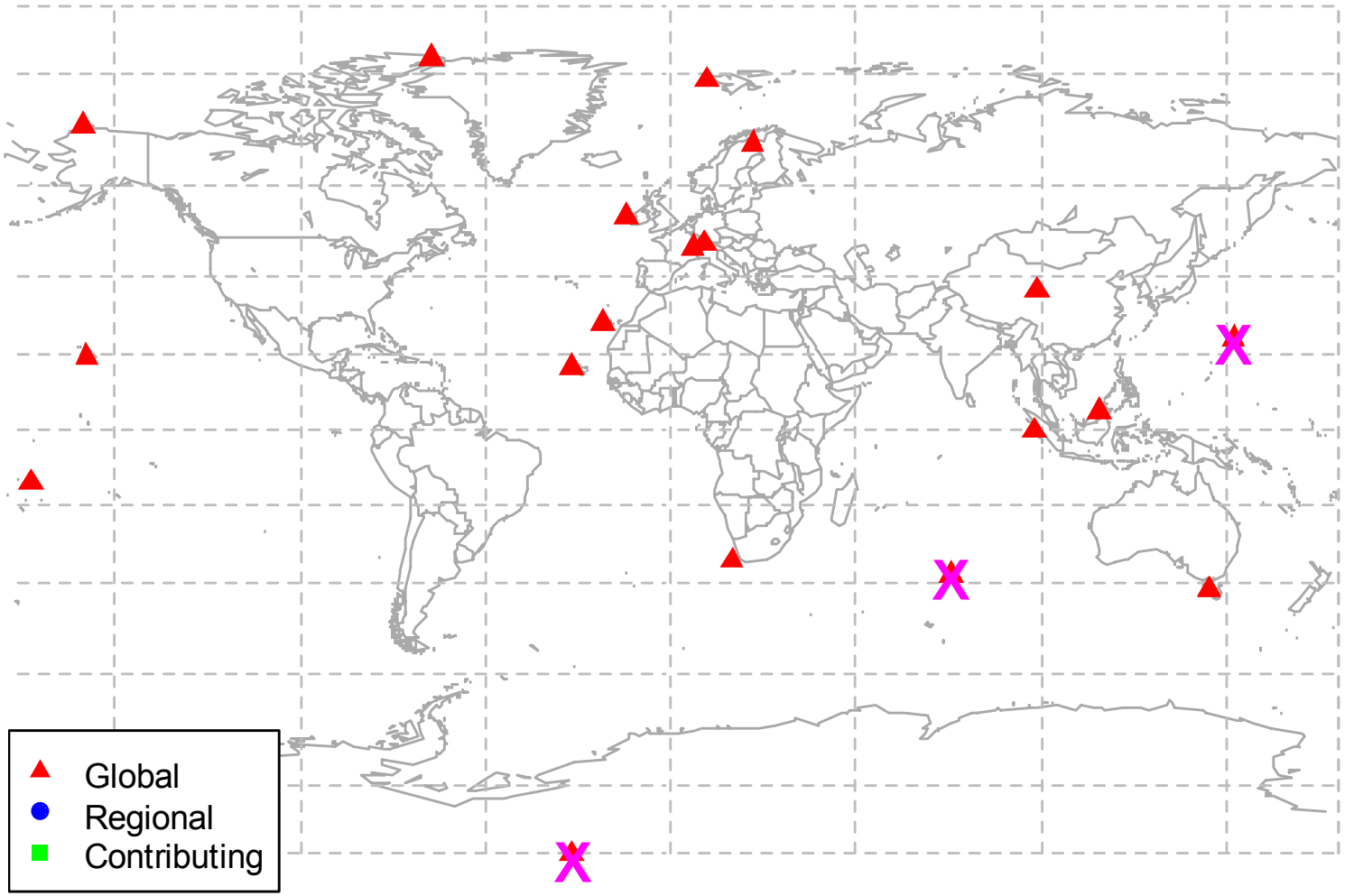
A **performance audit** is a voluntary check for conformity of a measurement where the audit criteria are the DQOs [data quality objectives] for that parameter. In the absence of formal DQOs, an audit will at least involve ensuring the traceability of
measurements to the Reference Standard.

[GAW Strategic Plan 2007-2011]

Global Network of Continuous CO_2 Observations



GAW stations in scope of WCC-CO_2



X: audit not feasible

System Audit

Document Title
AUDIT QUESTIONNAIRE FOR SYSTEM ... ATMOSPHERIC TRACE GAS MEASUR...

Version
Version 1.3-2006...

Contributors
J. Klausen (QA/S...

Approval
SAG Greenhous...
SAG Reactive G...

Scope
This document ... gas measureme... use during audi... and/or continuo... and N_2O.

Definitions
According to th... *audit* is defined ... are the DQOs ... ensuring the tr... generally defir... QA system. Th... evolves.

Summary Ranking of Pallas Station

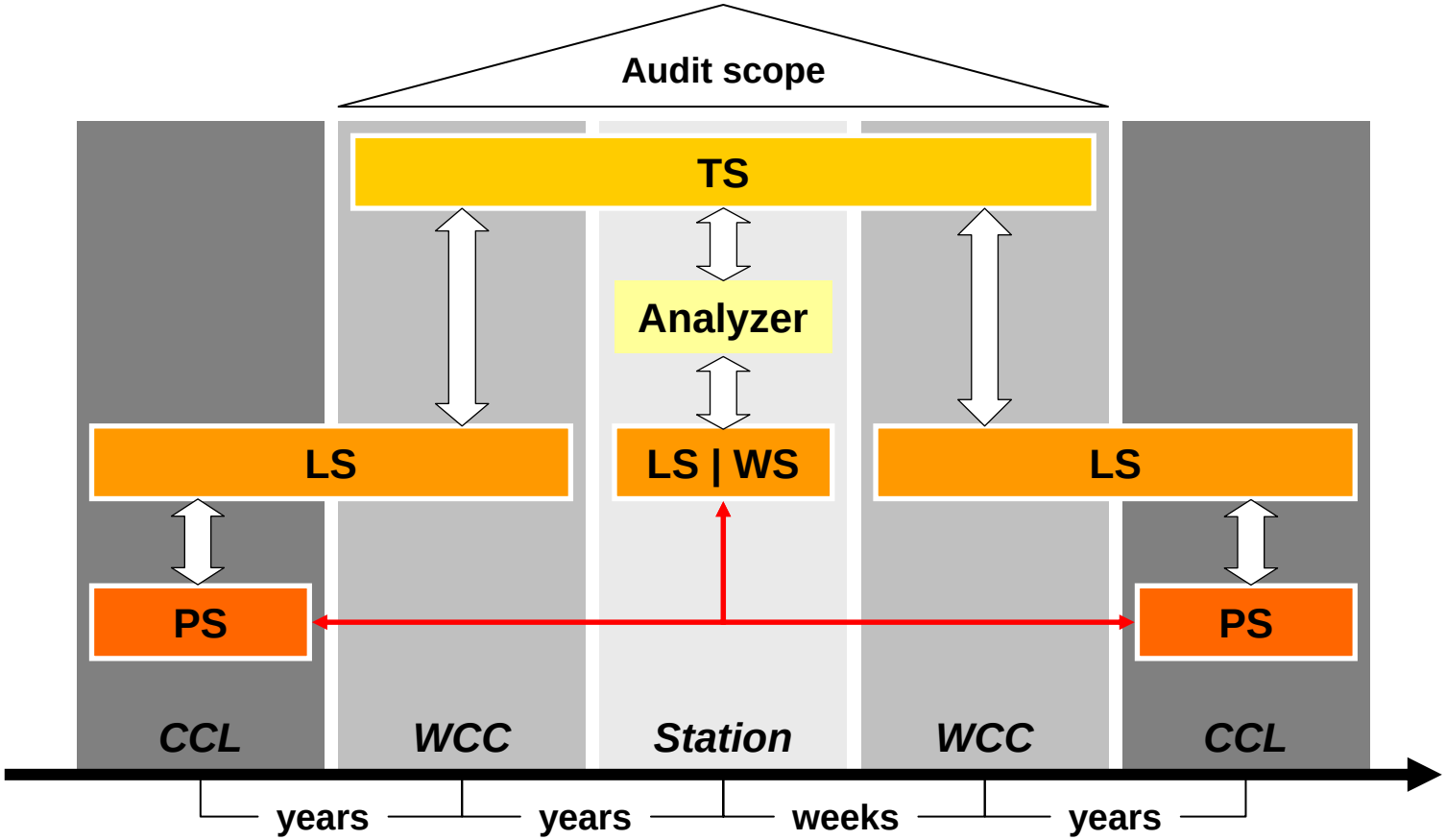
System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access possible
Facilities		
Laboratory and office space	(5)	State-of-the-art
Air Conditioning	(4)	...emperature changes
Power supply		
Internet access		...nection speed
...		...-art
...		...N
...		...I
...		..., SO_2, NO, NO_y,
...		... programme
...		(off site)
...		...ded
...	(3)	Not all data submitted yet

... to GAWSIS (www.empa.ch/gaw/gawsis) for a complete overview of measured

Site		Compound
Date of Audit	Auditor	

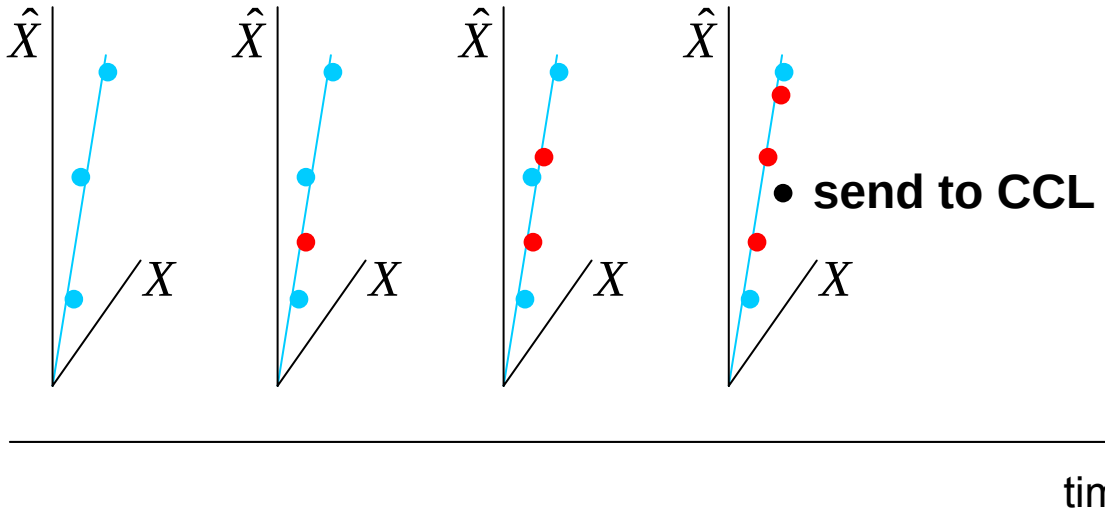
PARTS OF THIS QUESTIONNAIRE

Performance Audits and Traceability Chain



Traceability of WCC-CO_2 Lab Standards to CCL

- Currently, 3 NOAA certified standards
- Purchase 4 more in 2009
- Purchase 1-2 more every year
  - Maintain a range of 250 ~ 1000 ppbv CO_2
- Participate in round-robin exercises
- Constantly assess internal consistency of standards
- Return dubious standards to NOAA for re-calibration / re-certification



Isotope Issues

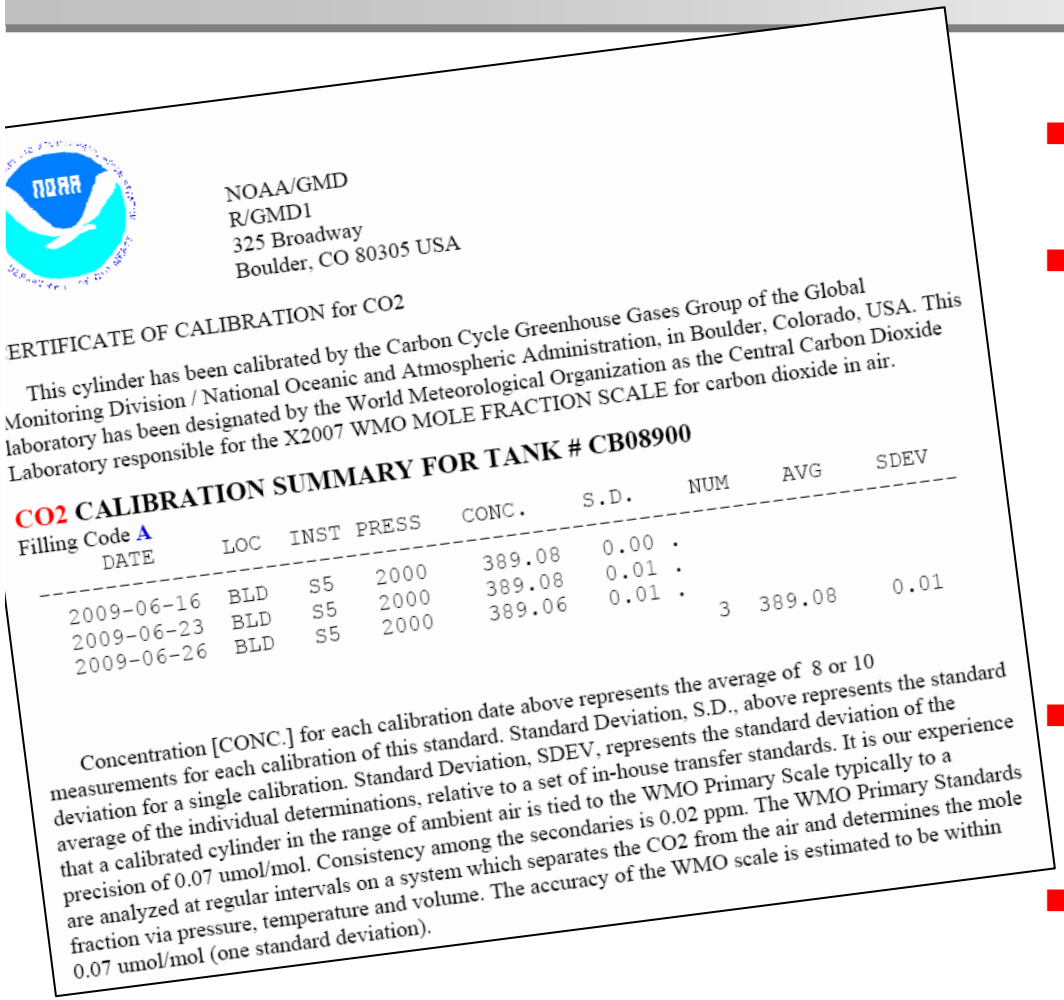
- Issues
  - Picarro CO_2 analyzer sensitive to ^{12}C only
  - NOAA CO_2 standards certified for total CO_2 and $\delta^{13}C$ not necessarily the same in all of them
  - Transfer of calibration to travelling standards needs correction

- Approach (still to be refined)
  - Characterize $\delta^{13}C$ in cylinders using TDLS system available at Empa

See P16, Werner et al.

  - Use LICOR NDIR instrument in addition to Picarro
  - Evaluate inter-comparison data considering type of instrument involved

Uncertainty of CCL Standards – What's in a word?



NOAA/GMD
R/GMD1
325 Broadway
Boulder, CO 80305 USA

ERTIFICATE OF CALIBRATION for CO2

This cylinder has been calibrated by the Carbon Cycle Greenhouse Gases Group of the Global Monitoring Division / National Oceanic and Atmospheric Administration, in Boulder, Colorado, USA. This laboratory has been designated by the World Meteorological Organization as the Central Carbon Dioxide Laboratory responsible for the X2007 WMO MOLE FRACTION SCALE for carbon dioxide in air.

CO2 CALIBRATION SUMMARY FOR TANK # CB08900

Filling Code A

DATE	LOC	INST	PRESS	CONC.	S.D.	NUM	AVG	SDEV
2009-06-16	BLD	S5	2000	389.08	0.00			
2009-06-23	BLD	S5	2000	389.08	0.01			
2009-06-26	BLD	S5	2000	389.06	0.01	3	389.08	0.01

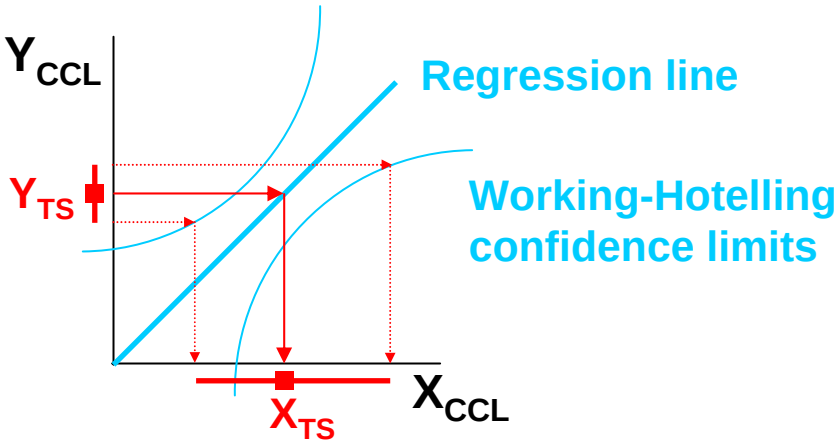
Concentration [CONC.] for each calibration date above represents the average of 8 or 10 measurements for each calibration of this standard. Standard Deviation, S.D., above represents the standard deviation for a single calibration. Standard Deviation, SDEV, represents the standard deviation of the average of the individual determinations, relative to a set of in-house transfer standards. It is our experience that a calibrated cylinder in the range of ambient air is tied to the WMO Primary Scale typically to a precision of 0.07 umol/mol. Consistency among the secondaries is 0.02 ppm. The WMO Primary Standards are analyzed at regular intervals on a system which separates the CO2 from the air and determines the mole fraction via pressure, temperature and volume. The accuracy of the WMO scale is estimated to be within 0.07 umol/mol (one standard deviation).

- Use of non-ISO terminology (formal issue)
- Certificate makes statements of reproducibility and repeatability
  - Okay for the CCL, but not useful for the user
  - Individual results should be used by the CCL to evaluate structure of residuals (e.g., drift); if residuals are okay, all data should be pooled
- Statements concerning other aspects of uncertainty are unclear (at least to me …)
- Present certificates make proper estimates of uncertainty difficult.

A (more) rigorous statement of uncertainties is needed in the certificate.

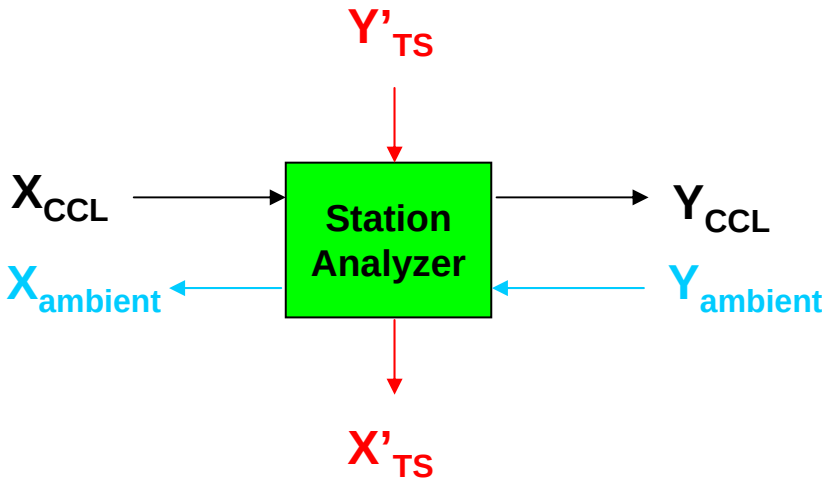
$$X_{CCL} = nnn.nn \pm ? \text{ ppm } (k = 2)$$

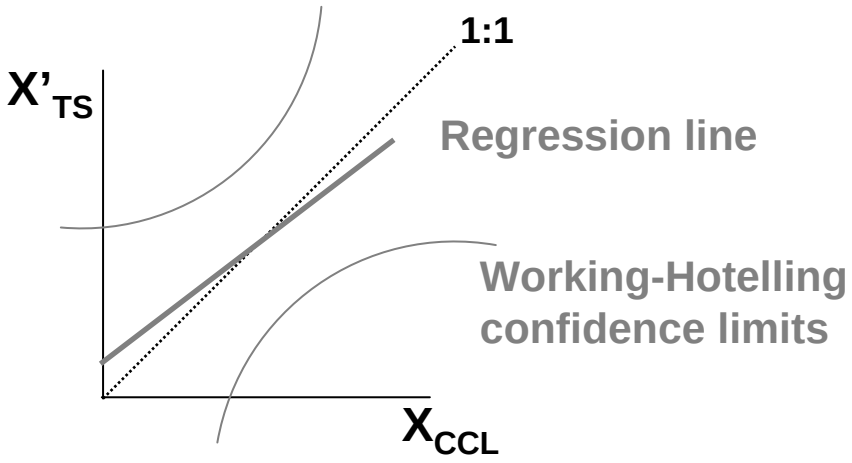
Uncertainty of Travelling Standards (TS)



- Calibration of transfer instrument using CCL standards
  - Fit slope and intercept (`fitexy`)
  - Construct Working-Hotelling confidence interval for regression line
- (Inverse) prediction of travelling standards
  - Compute statistics of repeated measurements Y_{TS}
  - Invert regression line to get X_{TS}
  - Use confidence bands to obtain confidence limits

Evaluation of Station Analyzer (SA)





- Challenge station analyzer with TS
- Return travelling standards to WCC and check stability
  - Pool TS calibration data
- Evaluate measurements conducted at station
  - Fit slope and intercept (`fitexy`)
  - Construct Working-Hotelling confidence interval for regression line
  - Evaluate uncertainties determined at station
    - repeatability, drift of analyzer
  - Evaluate bias of analyzer against DQOs
    - Issues with calibration

Conclusions

- System audits
  - offer a ‘second opinion’ and
  - provide documentation of procedures and design of system
- Performance audits
  - offer an additional means of ensuring traceability to the CCL
  - help unveil and resolve ‘issues’ with calibration
  - are evaluated using a rigorous statistical approach
- Travelling standards
  - carry a somewhat larger uncertainty than CCL lab standards
  - bring an entire set of ‘fresh’ standards to a station
- Personal exchange of experience during an audit
  - improves the quality of the observing systems
  - fosters identification of observers with their work
  - gives recognition to the work at the station

- Assessment of uncertainty of observations requires more rigorous statements of uncertainty of CCL standards

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Acknowledgement

- Financial support from MeteoSwiss