Quality Assurance and Quality Control for Trace Gas Observations within GAW

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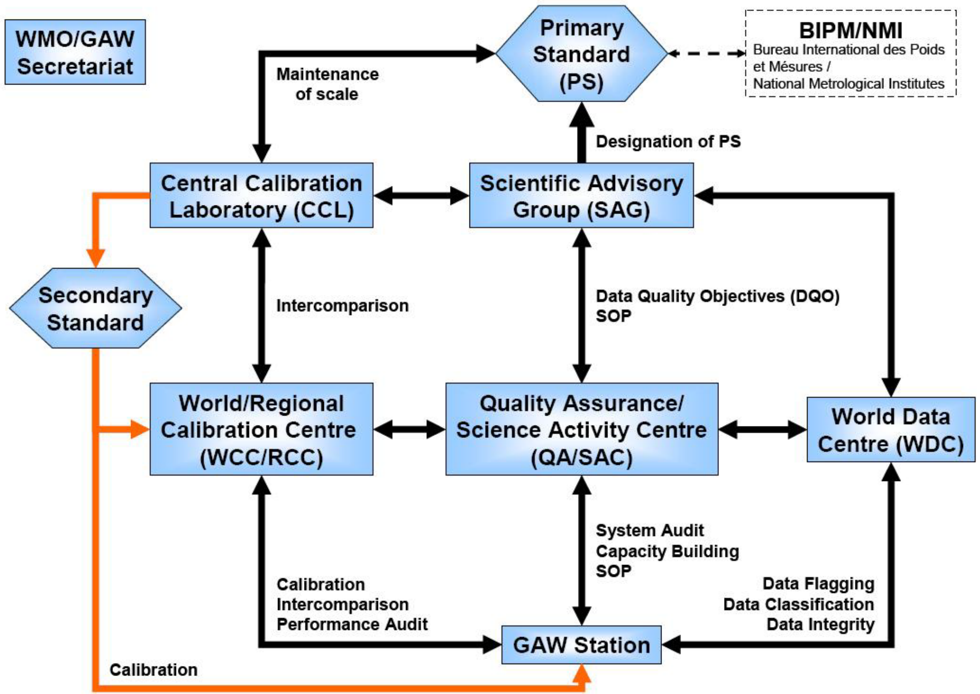
with contributions from NOAA-ESRL, ICOS & WCC-Empa

2018 Meeting of the Science Advisory Group for Aerosols, Geneva, 10 July 2018

Empa
Materials Science and Technology

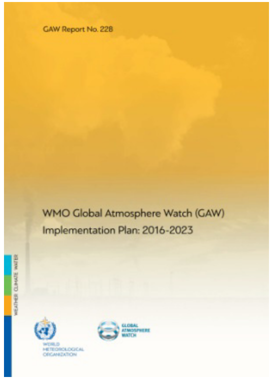
GAW Quality Management Framework

Elements of the Quality Assurance system,
QA activities and workflow in GAW



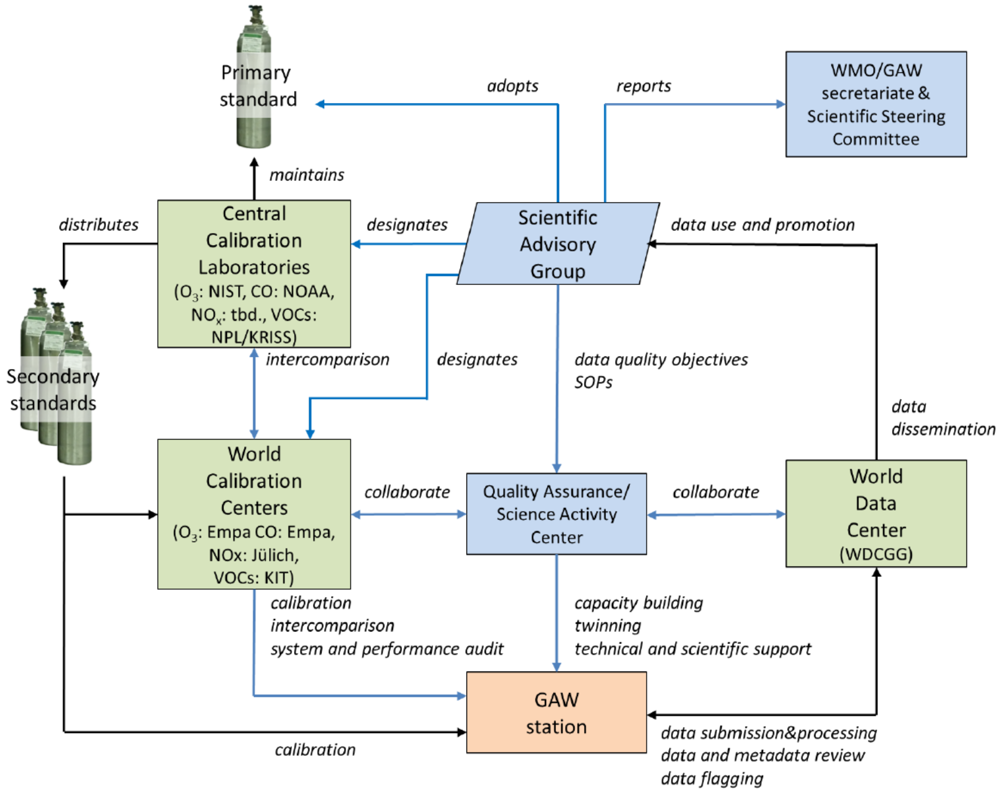
map of GAW stations

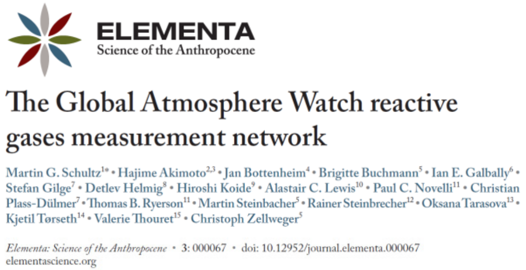
https://gawsis.meteoswiss.ch



GAW Implementation Plan 2016-2023,
GAW Report Nr. 228, 2017

Quality Management Framework for Reactive Gases





ELEMENTA
Science of the Anthropocene

The Global Atmosphere Watch reactive gases measurement network

Martin G. Schultz[1*] • Hajime Akimoto[2,3] • Jan Bottenheim[4] • Brigitte Buchmann[5] • Ian E. Galbally[6] • Stefan Gilge[7] • Detlev Helmig[8] • Hiroshi Koide[9] • Alastair C. Lewis[10] • Paul C. Novelli[11] • Christian Plass-Dülmer[7] • Thomas B. Ryerson[11] • Martin Steinbacher[5] • Rainer Steinbrecher[12] • Oksana Tarasova[13] • Kjetil Tørseth[14] • Valerie Thouret[15] • Christoph Zellweger[5]

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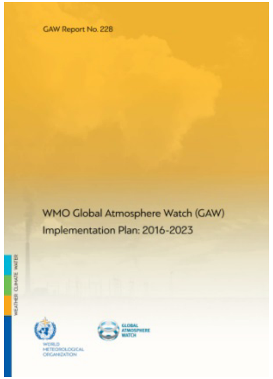
elementascience.org

Schultz et al., Elementa, 2015

GAW's Central Facilities – the Trace Gas Perspective

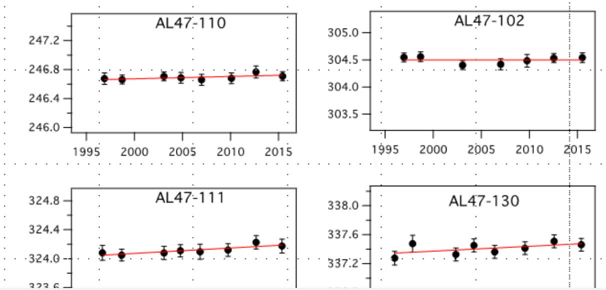
GAW Central Facilities

Variable	Quality Assurance / Science Activity Centre	Central Calibration Laboratory	World Calibration Centre	Regional Calibra-tion Centres	World Data Centre
CO_2	JMA (Asia, South-West Pacific)	NOAA-ESRL	NOAA-ESRL (round robin) Empa (audits)		JMA
CO_2 Isotopes		MPI-BGC			JMA
CH_4	Empa (Americas, Europe, Africa) JMA (Asia, South-West Pacific)	NOAA-ESRL	Empa (Americas, Europe, Africa) JMA (Asia, South-West Pacific)		JMA
N_2O	UBA	NOAA-ESRL	KIT/IMK-IFU		JMA
SF_6		NOAA ESRL	KMA-KGAWC		JMA
CFCs, HCFCs, HFCs					JMA
Surface Ozone	Empa	NIST	Empa	OCBA (South America)	NILU
CO	Empa	NOAA-ESRL	Empa		JMA
VOCs	UBA	NPL (Ethane, Propane, n-butane, n-pentane, Acetylene, Toluene, Benzene, Isoprene) NIST (monoterpenes)	KIT/IMK-IFU		NILU
NO_X	UBA	NPL (NO)	FZJ (IEK-8) (NO)		NILU
SO_2					NILU



GAW Implementation Plan 2016-2023,
GAW Report Nr. 228, 2017

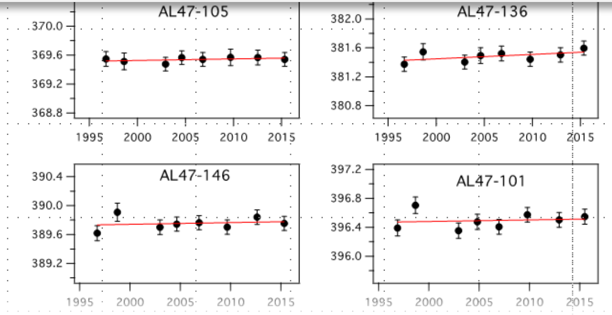
Example – CCL for CO2 (NOAA-ESRL)



Drift Assessment

	CO2	drift rate (ppm/yr)	Unc. 2-sd	N
AL47-110	246.69	0.0028	0.0099	8
AL47-102	304.45	0.0006	0.0144	7
AL47-111	324.11	0.0077	0.0133	8
AL47-130	337.41	0.0081	0.0133	8
AL47-106	412.25	0.0087	0.0169	8
AL47-123	423.27	0.0034	0.0158	8
AL47-107	453.25	-0.0099	0.0174	6
ND17440	479.74	0.0076	0.0456	5
AL47-132	521.7	0.0101	0.0201	8

For greenhouse gases, primary standards are prepared gravimetrically by mixing aliquots of pure gaseous or liquid reagents with ultra-pure air,
and are calibrated manometrically by measuring temperature and pressure in well-defined volumes of the whole air and the cryogenically trapped species of interest.



Mean: 0.05 ppm/decade

slide: courtesy of Brad Hall (NOAA)

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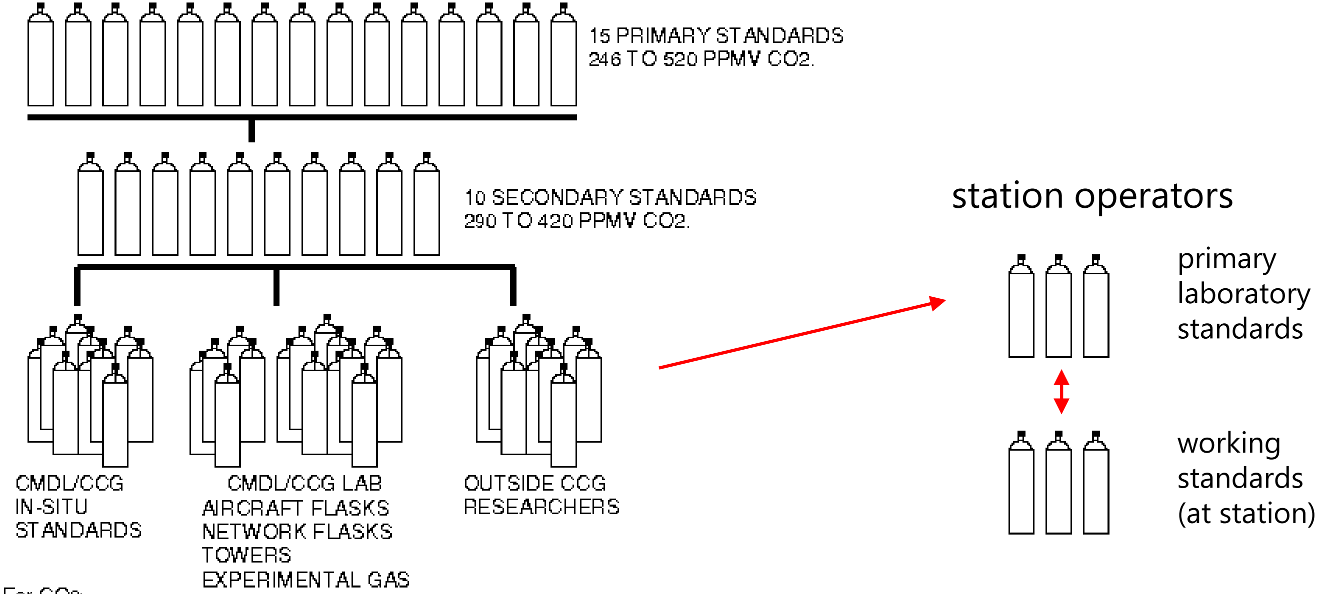
Propagation of the scale at CCL



For CO_2:
CALIBRATION PRECISION; 0.014 µmol/mol [1 sd of calibrations < 6 months apart].
precision for < 325 approx. 0.1
precision for > 425 approx. 0.25

Absolute Uncertainty; 0.1 µmol/mol
Internal consistency [325-425 µmol/mol]; 0.04 µmol/mol [2 sigma] [< 2 years]

https://www.esrl.noaa.gov/gmd/ccl/airstandard.html

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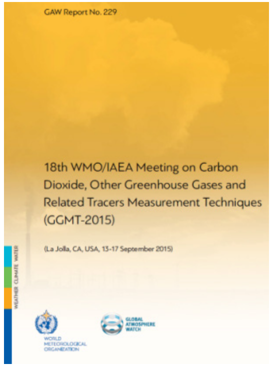
Targeted compatibility for CO2 within GAW

Recommended compatibility of greenhouse gas measurements

Component	Compatibility goal 1-sigma	Extended compatibility goal[1]	Range in unpolluted troposphere (approx. range for 2015)	Range covered by the WMO scale
CO_2	± 0.1 ppm (North.Hem.) ± 0.05 ppm (So.Hemisph)	± 0.2 ppm	380 - 450 ppm	250 – 520 ppm
CH_4	± 2 ppb	± 5 ppb	1750 – 2100 ppb	300 – 5900 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	30 -500 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	325 – 335 ppb	260 – 370 ppb
SF_6	± 0.02 ppt	± 0.05 ppt	8 – 10 ppt	2.0 – 20 ppt
H_2	± 2 ppb	± 5 ppb	400 – 600 ppb	140 –1200 ppb
$\delta^{13}C\text{-}CO_2$	± 0.01‰	± 0.1‰	-9.5 to -7.5‰ (VPDB)	
$\delta\,^{18}O\text{-}CO_2$	± 0.05‰	± 0.1‰	-2 to +2‰ ($VPDB\text{-}CO_2$)	
$\Delta^{14}C\text{-}CO_2$	± 0.5‰	± 3‰	-50 to 50‰	
$\Delta\,^{14}C\text{-}CH_4$	± 0.5‰		50-350‰	
$\Delta\,^{14}C\text{-}CO$	± 2 molecules cm^{-3}		0-25 molecules cm^{-3}	
$\delta\,^{13}C\text{-}CH_4$	± 0.02‰	± 0.2‰		
δ D-CH_4	± 1‰	± 5‰		
O_2/N_2	± 2 per meg	± 10 per meg	-900 to -400 per meg (vs. SIO scale)	



GGMT-2015 Report,
GAW Report Nr. 229, 2016

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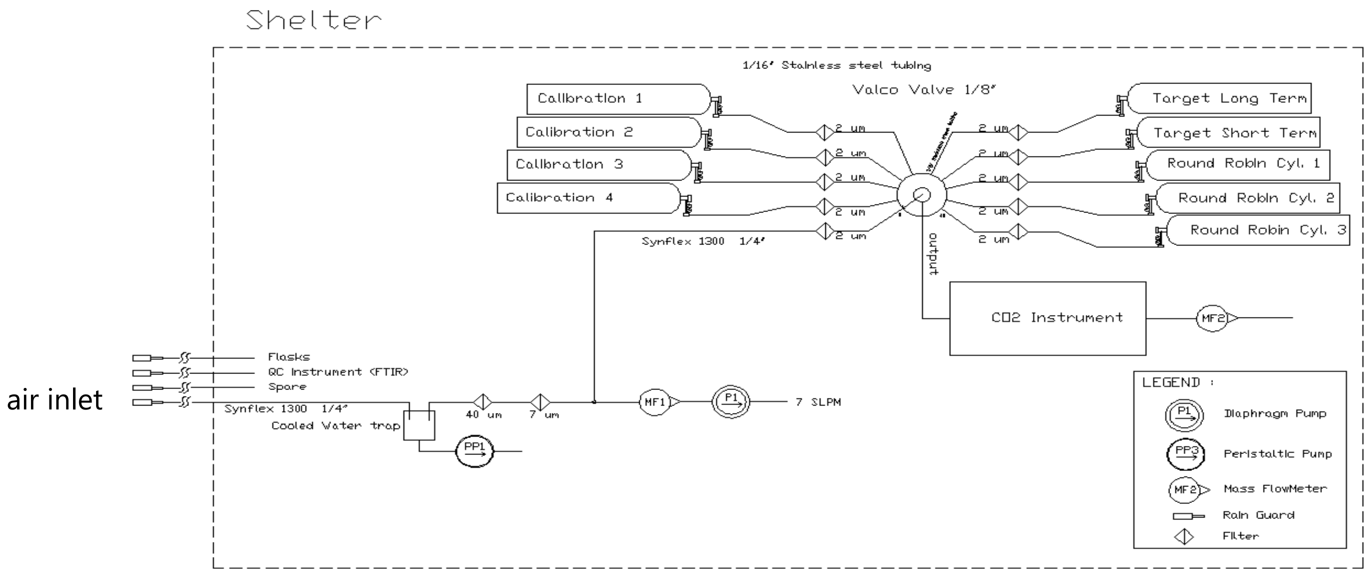
Typical plumbing design for CO2 observations

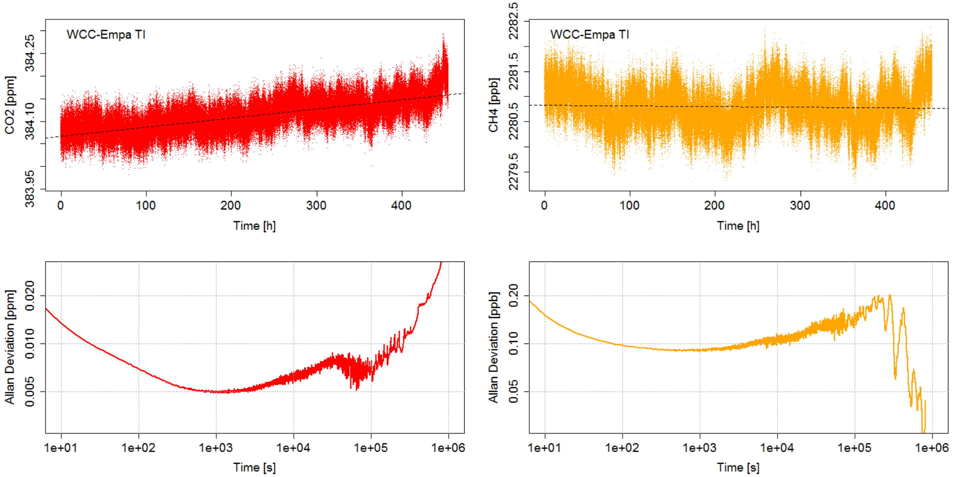


ICOS Atmospheric Station Specification Document
https://www.icos-ri.eu/documents/ATC%20Public

Frequency of calibrations depending on the time-scale of sensitivity changes of the analyzer

Calibration frequency for CO2 observations

Allan deviation plots



Zellweger et al., AMT, 2016

"A thorough analysis of the CO2 and CH4 stability of [this type of cavity enhanced laser spectrometer] indicates that the optimal calibration frequency is approximately 30 h."

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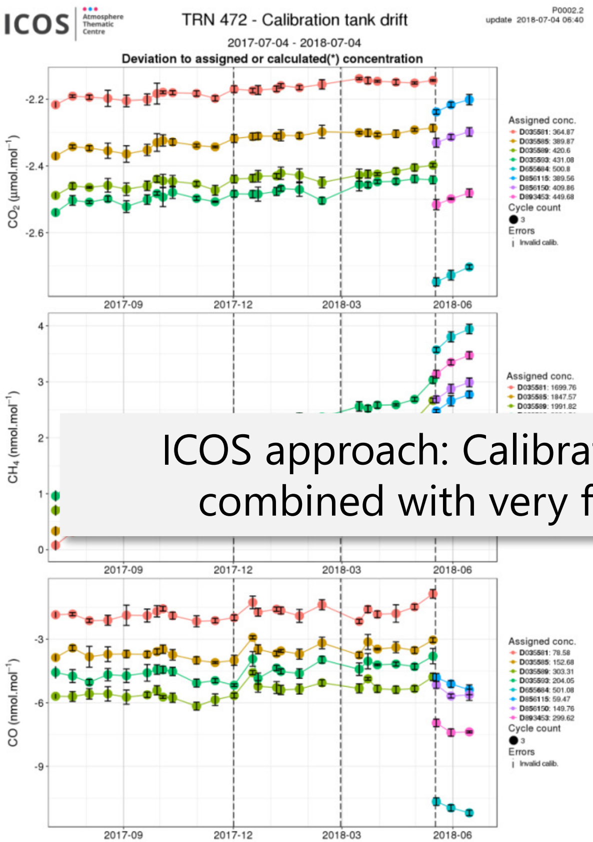
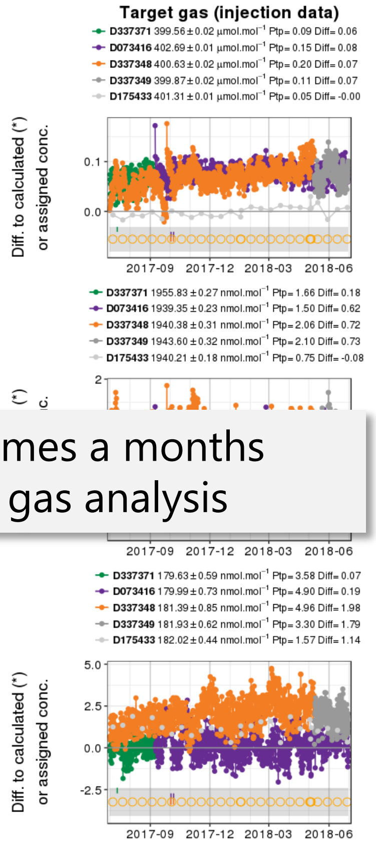
Calibration frequency for CO2 observations





ICOS approach: Calibration only 2-3 times a months combined with very frequent target gas analysis

ICOS ATC (Atmospheric Thematic Center), screenshots

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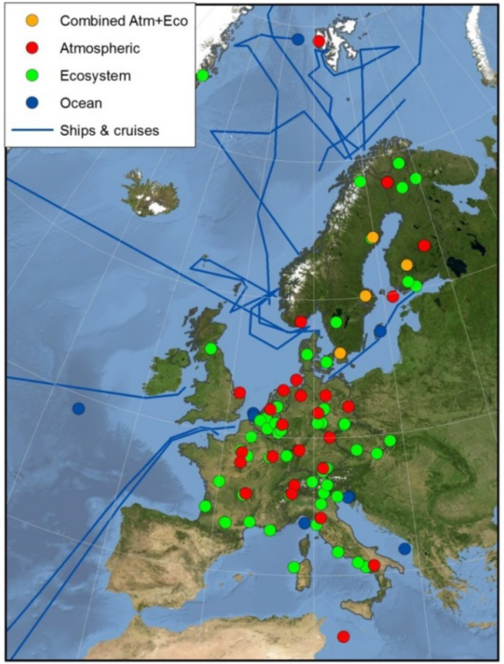
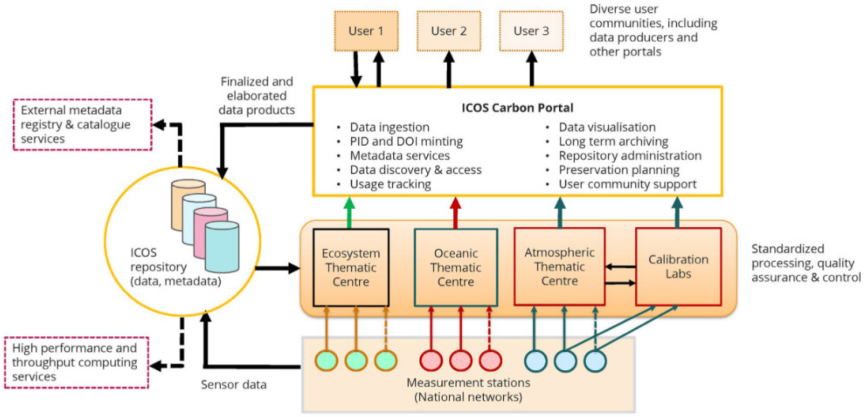
Towards strong standardization within Europe

- the Integrated Carbon Observation System (ICOS) example

ICOS: a pan-European research infrastructure which provides harmonized and high precision data on carbon cycle and greenhouse gas budget and perturbations



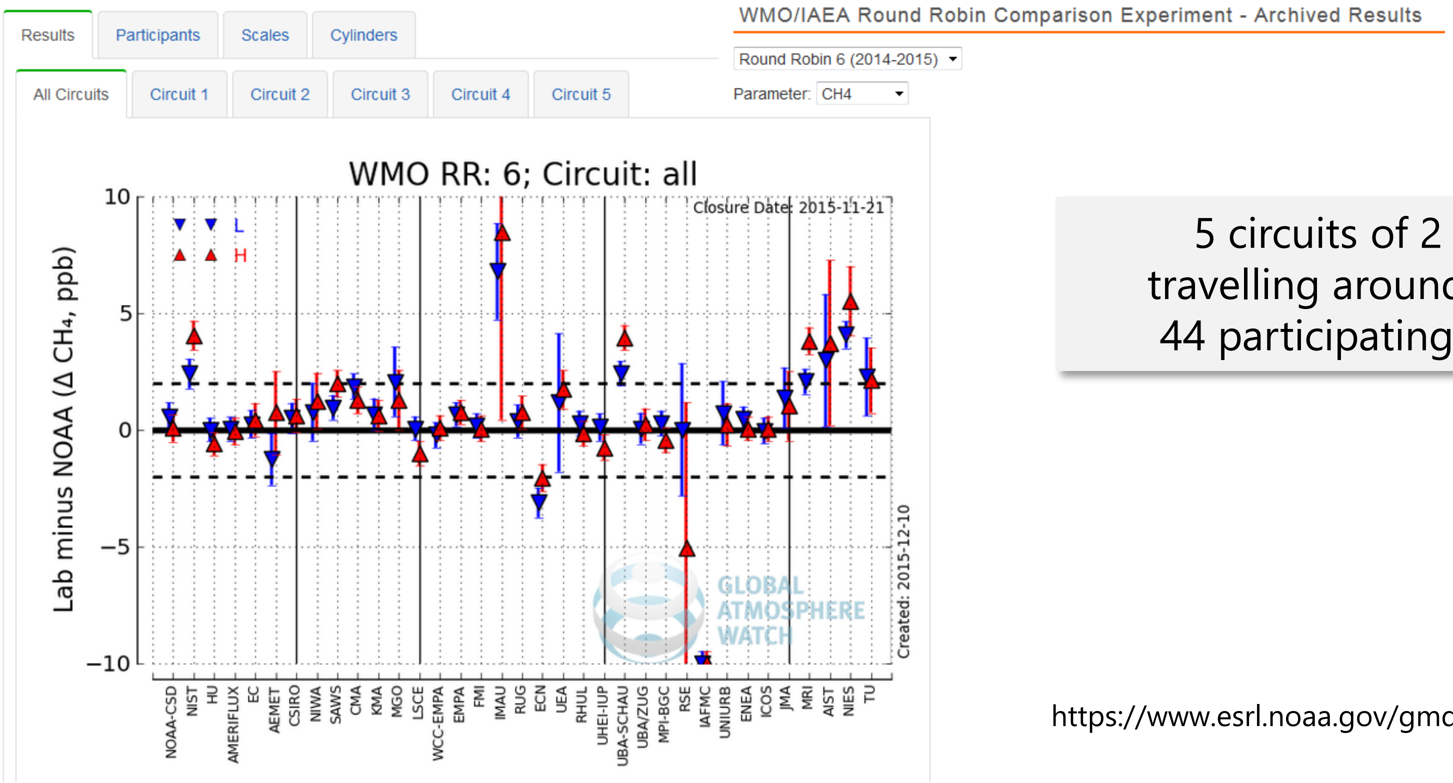


https://www.icos-cp.eu

- standardized instruments and procedures
- central provision of reference gases
- central data processing and data dissemination

Network wide quality control

- Round Robin Exercises for Greenhouse Gases

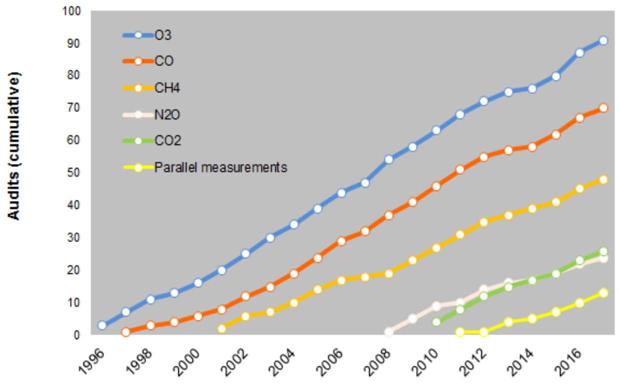


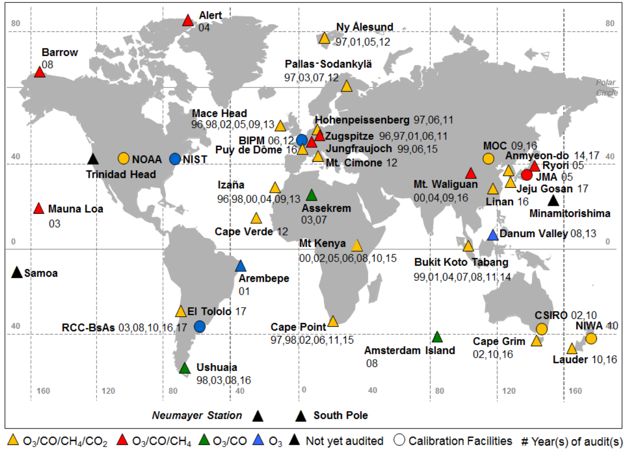
5 circuits of 2 cylinders travelling around the world; 44 participating labs (RR6)

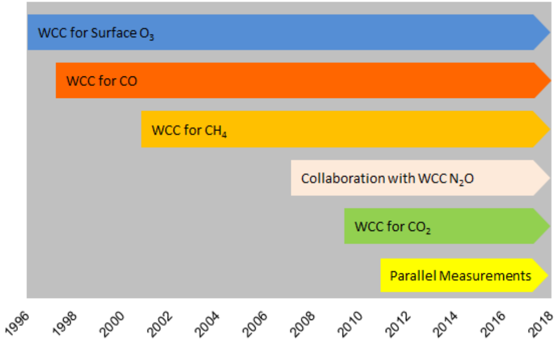
https://www.esrl.noaa.gov/gmd/ccgg/wmorr/

Network wide quality control

- World Calibration Centre for Surface O3, CO, CH4, and CO2 (WCC-Empa)







- established in 1996, more than 90 audits since then
- ensures traceability to the GAW reference and determines compatibility
- assists stations with regards to instruments and measurement issues (WCC-Empa & QA/SAC-CH)
- improves technical know-how at stations through on-site training (WCC-Empa & QA/SAC-CH)

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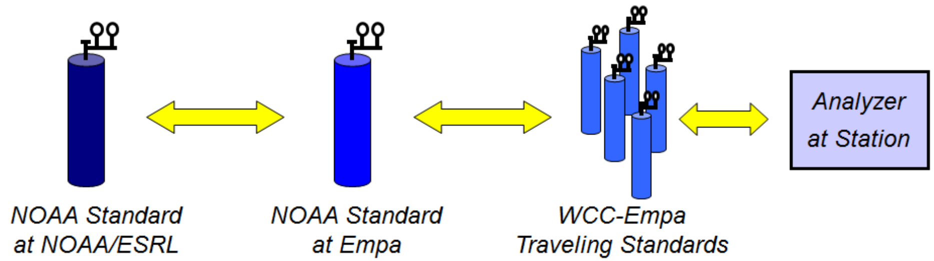

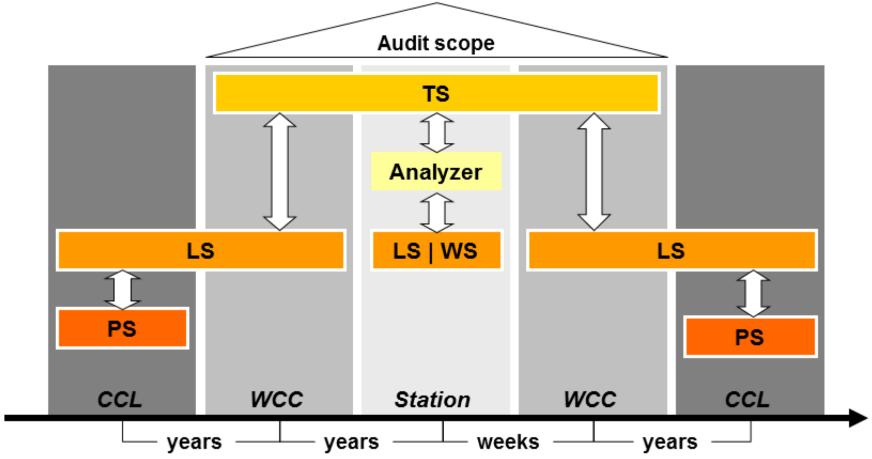

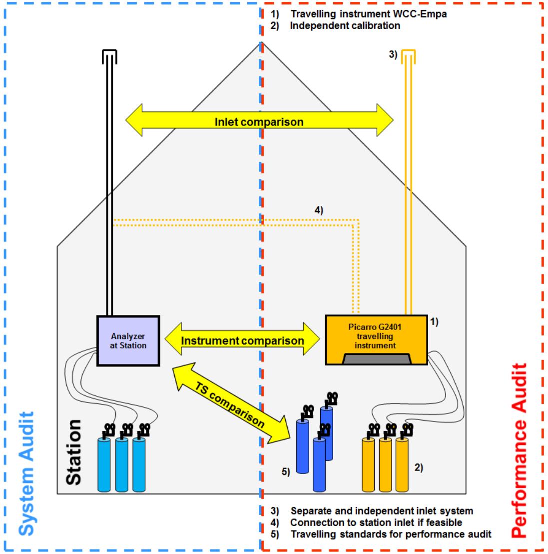

https://www.empa.ch/web/s503/wcc-empa

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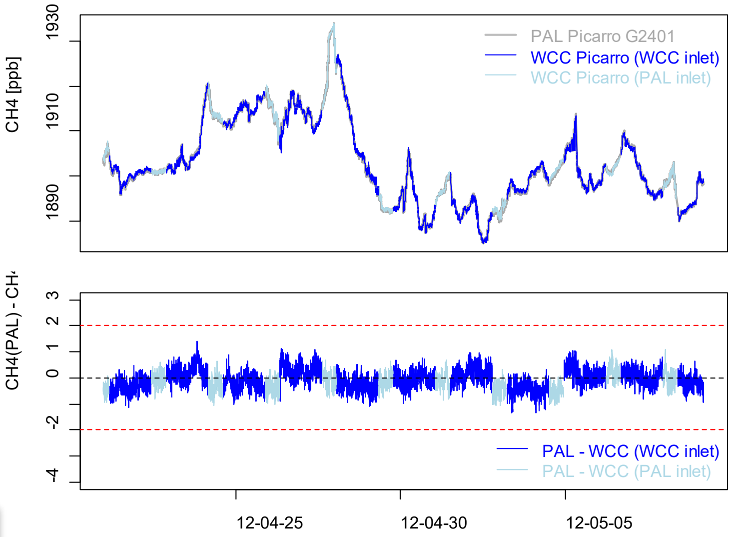
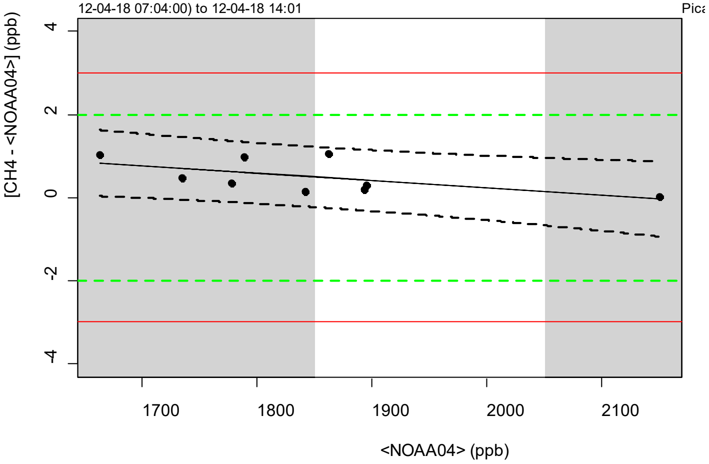
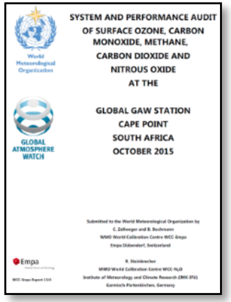


WCC-Empa audit in Pallas (Finland)
(April 2012)





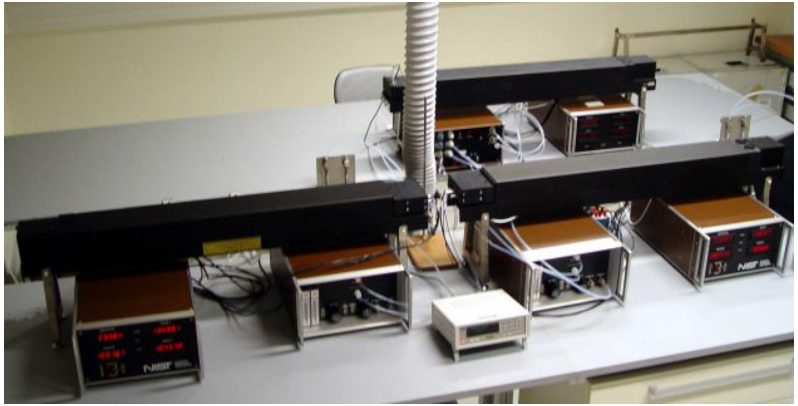
SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE, CARBON DIOXIDE AND NITROUS OXIDE AT THE

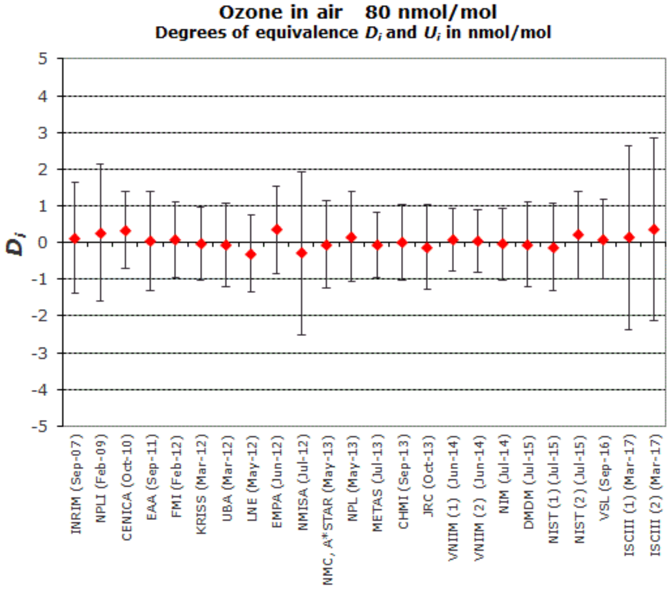
GLOBAL GAW STATION CAPE POINT SOUTH AFRICA OCTOBER 2015

Audit reports are publicly available at
https://gawsis.meteoswiss.ch/
www.empa.ch/gaw, and
http://www.wmo.int/pages/prog/arep/gaw/other_pub.html

Traceability for surface ozone measurements

- Each NIST Standard Reference Photometer (SRP) is a realisation of a Primary Standard
- CCL is NIST, which maintains SRP#2 (=reference for GAW), but SRP#X is also a primary standard
- The 'SRP family', which defines the O_3 reference, is inter-compared in an ongoing Key Comparison organized by BIPM (www.bipm.org)





Calibration (and auditing) of surface O3 analyzers

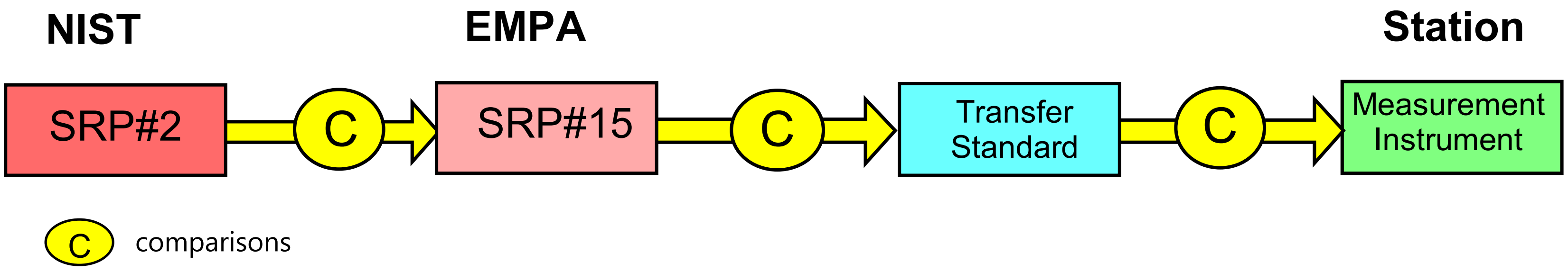
Reference: Standard Reference Photometer (SRP)

World reference: SRP #2 at National Institute for Standards and Technology

Currently: approx. 60 SRPs worldwide

Transfer standard / calibrator is calibrated against a reference photometer and used for the calibration of ozone instruments

Traceability chain:



Measurement uncertainty

Table 1 - Example of an uncertainty budget of an ozone analyser

Component (*y*)	Source	Distribution	Contribution to *u(x)*
Imperfect calibration / linearity	Comparison between TS and OA	Rectangular	$0.0017 \cdot x^*$
Repeatability	Instrument stability	Rectangular	$0.0016 \cdot x$
Span drift	Instrument stability	Rectangular	$0.0040 \cdot x$
Zero drift	Instrument stability	Rectangular	0.17
Pressure *P*	Pressure measurement	Rectangular	$0.0002 \cdot x$
Temperature *T*	Temp. measurement	Rectangular	$0.0005 \cdot x$
H_2O interference	Interference in the UV		$0.0060 \cdot x$
Other interferences	Interference in the UV		0.6
Sampling loss (Inlet)	Inlet material, dirt	Rectangular	$0.0014 \cdot x$

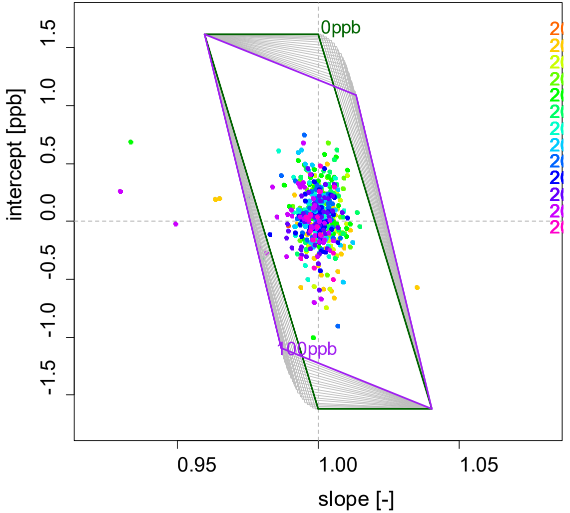
* *where x refers to ozone mole fraction*

A conservative estimate of the total uncertainty can now be obtained by combing the uncertainties of the ozone analyser (13), the transfer standard (12) and the primary reference (11).

$$u(O_3) = \sqrt{(0.81)^2 + (0.0089 \times O_3)^2} \text{ nmol mol}^{-1} \qquad (14)$$

O3 measurement guidelines, GAW Report Nr. 209, 2013

Intercept vs. slope plot for 559 calibrations of various ozone analysers with transfer standards within the Swiss National Air Pollution Monitoring Network between November 2005 and April 2017

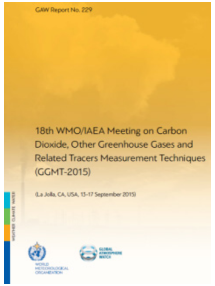


Tarasick et al., in prep.

Conclusions

- Central Facilities are assigned for most of the trace gases targeted in GAW
- Traceability chains and network wide quality control activities are in place
- Maximum possible homogenization of the observations vs.

"WMO recognizes the importance of <u>independent</u> measurement methods, calibration scales and calibration techniques that are consistent with the data quality objectives quality control, transparency and traceability defined elsewhere in this document. The goal of this diversity is to assure that the global atmospheric measurement enterprise remains robust and less vulnerable to systematic or method-specific error. A key component of this diversity is the rigorous and frequent comparison of independent methods."



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