Quality Control of Trace Gas Observations

Martin Steinbacher

Empa, Laboratory for Air Pollution / Environmental Technology & GAW Quality Assurance/Scientific Activity Centre (QA/SAC Switzerland), Dübendorf, Switzerland

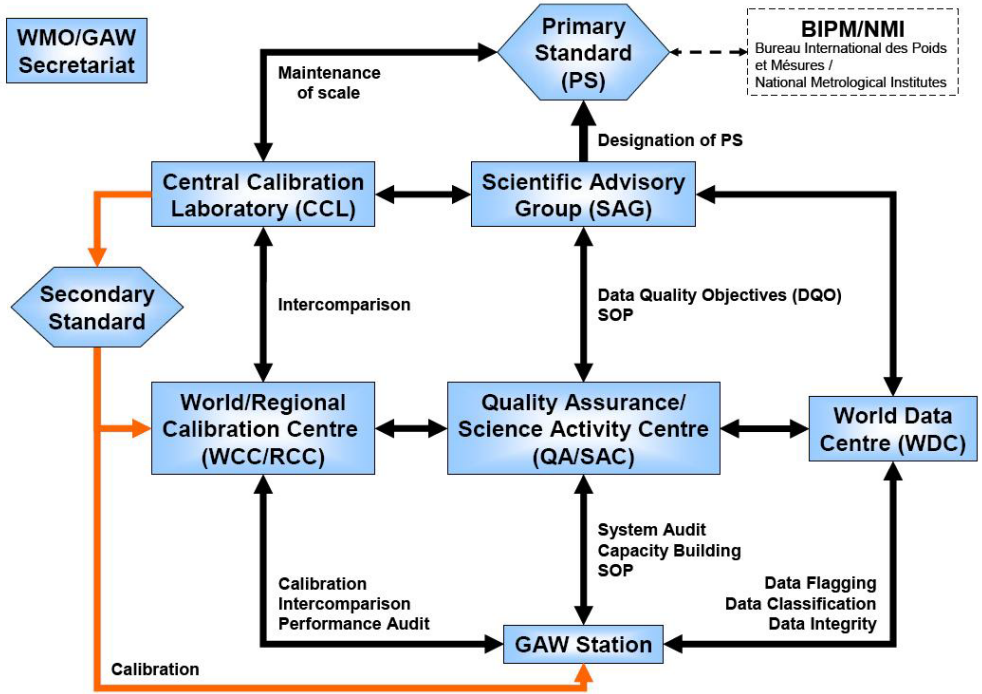
with contributions from NOAA-ESRL, ICOS & WCC-Empa

School of Atmospheric Measurements in Latin America and the Caribbean (SAMLAC)
Puerto Rico, 12 November 2018

Empa
Materials Science and Technology

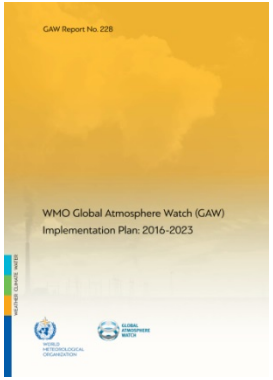
GAW Quality Management Framework

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



map of GAW stations

https://gawsis.meteoswiss.ch

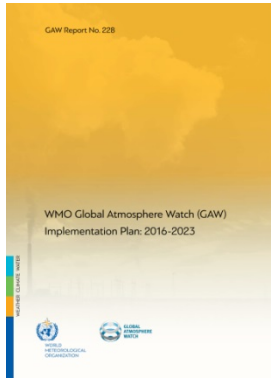


GAW Implementation Plan 2016-2023,
GAW Report Nr. 228, 2017

GAW's Central Facilities – the Trace Gas Perspective

GAW Central Facilities

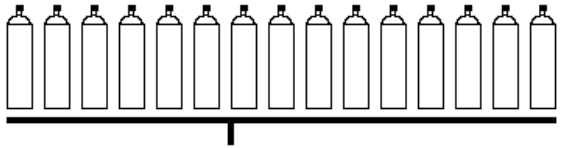
Variable	Quality Assurance / Science Activity Centre	Central Calibration Laboratory	World Calibration Centre	Regional Calibration Centres	World Data Centre
CO_2	JMA (Asia, South-West Pacific)	NOAA-ESRL	NOAA-ESRL (round robin) Empa (audits)		JMA
CO_2 Isotopes		MPI-BGC			JMA
CH_4	Empa (Americas, Europe, 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



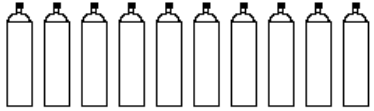
GAW Implementation Plan 2016-2023,
GAW Report Nr. 228, 2017

Propagation of the scale, from CCL to station

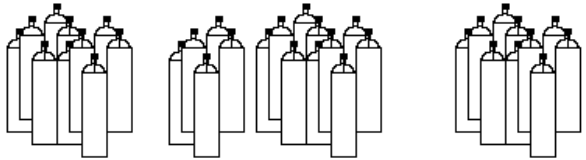
Central Calibration Laboratory



15 PRIMARY STANDARDS
246 TO 520 PPMV CO2.



10 SECONDARY STANDARDS
290 TO 420 PPMV CO2.

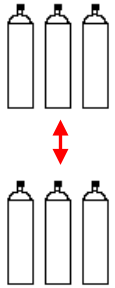


CMDL/CCG
IN-SITU
STANDARDS

CMDL/CCG LAB
AIRCRAFT FLASKS
NETWORK FLASKS
TOWERS
EXPERIMENTAL GAS

OUTSIDE CCG
RESEARCHERS

station operators



primary laboratory standards

working standards (at station)

For CO2:
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

Traceability

- make sure that you know your traceability chain
- add this information to your data / metadata

```
C01 TITLE: CO hourly mean data
C02 FILE NAME: tll330s00.dmc_empa.as.cn.co.nl.hr2014.dat
C03 DATA FORMAT: Version 1.0
C04 TOTAL LINES: 8792
C05 HEADER LINES: 32
C06 DATA VERSION: 201505
C07 STATION NAME: El Tololo
C08 STATION CATEGORY: Regional
C09 OBSERVATION CATEGORY: Air sampling observation at a stationary platform
C10 COUNTRY/TERRITORY: Chile
C11 CONTRIBUTOR: DMC Empa
C12 LATITUDE: -30.17254
C13 LONGITUDE: -70.79923
C14 ALTITUDE: 2220
C15 NUMBER OF SAMPLING HEIGHTS: 1
C16 SAMPLING HEIGHTS: 5
C17 CONTACT POINT: martin.steinbacher@empa.ch gtorres@meteochile.cl
C18 PARAMETER: CO
C19 COVERING PERIOD: 2014-01-01 2014-12-31
C20 TIME INTERVAL: hourly
C21 MEASUREMENT UNIT: ppb
C22 MEASUREMENT METHOD: Cavity ring-down spectroscopy (CRDS)
C23 SAMPLING TYPE: continuous
C24 TIME ZONE: UTC
C25 MEASUREMENT SCALE: WMO CO X2004
C26 CREDIT FOR USE: This is a formal notification for data users. "For scientific
C27 and provided without charge. By their use you accept that an offer of co-autho
C28 with the data providers or owners whenever substantial use is made of their da
C29 must be made to the data providers or owners and the data centre when these da
C30 COMMENT:
C31
C32    DATE  TIME        DATE  TIME         CO    ND      SD     F CS        REM
2014-01-01 00:00 9999-99-99 99:99      54.55    59    1.47 -9999  0 -99999999
2014-01-01 01:00 9999-99-99 99:99      54.72    60    1.41 -9999  0 -99999999
2014-01-01 02:00 9999-99-99 99:99      55.18    60    1.41 -9999  0 -99999999
2014-01-01 03:00 9999-99-99 99:99      56.24    60    1.40 -9999  0 -99999999
2014-01-01 04:00 9999-99-99 99:99      56.21    60    1.39 -9999  0 -99999999
2014-01-01 05:00 9999-99-99 99:99      56.03    60    1.66 -9999  0 -99999999
2014-01-01 06:00 9999-99-99 99:99      57.22    60    1.36 -9999  0 -99999999
```

El Tololo - DMC, Empa

Parameter Inventory | Parameter Metadata | Station | Contributor

CH_4 continuous | CO continuous | CO_2 continuous | O_3 continuous

Observation | Processing/Calibration | Contact Person | Reference | Data/Quick Plot

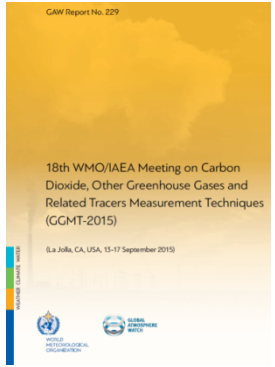
Current Scale	WMO CO X2004
Scale and Calibration (traceability)	the analyzer is regularly calibrated with four reference gases. All assigned mole fractions are reported on the WMO CO X2004 scale. The quality of the calibration is verified with a fifth reference gas (target cylinder).
Measurement Calibration	Four calibration tanks are measured automatically every 2 to 9 days. Three of them are tanks purchased from the GAW Central Calibration Laboratory (NOAA ESRL), the mole fractions of the fourth tank are determined by the GAW World Calibration Centre for CH_4, CO_2, CO and surface O_3 (WCC-Empa). WCC-Empa also assigned the mole fractions of an additional target cylinder that is measured every second day for quality control.
Data Processing	Quality assurance procedures involve time series plots, target tank (i.e. cylinders containing natural air with assigned trace gas mole fractions that are treated as (unknown) sample in a sequence of analyses) measurements, and consistency checks.
Processing for averaging	**Processing on hourly data :** high-resolution data are aggregated to 1min averages before hourly averages are calculated. Thus, ND (the number of detections) refers to the number of available 1min averages within the respective hour. **Processing on daily data :** hourly averages are aggregated to daily means. Thus, ND (the number of detections) refers to the number of available hourly averages within the respective day. **Processing on monthly data :** daily data are aggregated to monthly means. Thus, ND (the number of detections) refers to the number of available daily averages within the respective month.
Measurement Unit	ppb
Flag	

Targeted compatibility for greenhouse gases within GAW

Recommended compatibility of greenhouse gas measurements

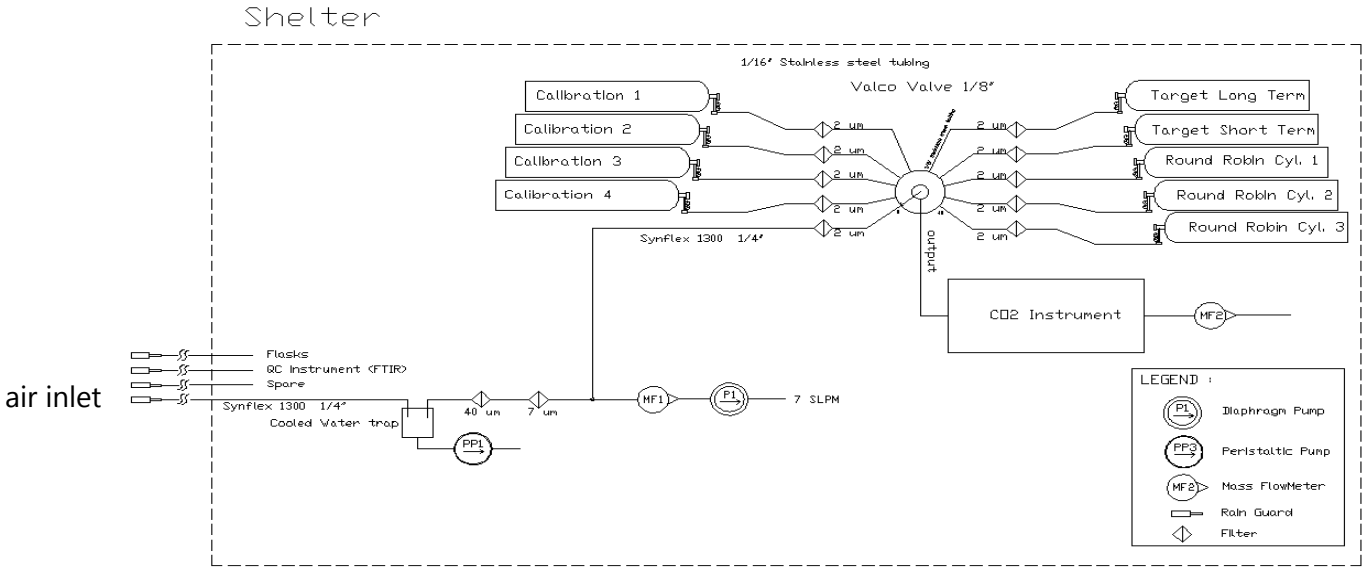
Component	*Compatibility goal 1-sigma*	*Extended compatibility goal*[1]	*Range in unpolluted troposphere (approx. range for 2015)*	*Range covered by the WMO scale*
CO_2	± 0.1 ppm (North.Hem.) ± 0.05 ppm (So.Hemisph)	± 0.2 ppm	380 - 450 ppm	250 – 520 ppm
CH_4	± 2 ppb	± 5 ppb	1750 – 2100 ppb	300 – 5900 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‰		
$\delta\ D\text{-}CH_4$	± 1‰	± 5‰		
O_2/N_2	± 2 per meg	± 10 per meg	-900 to -400 per meg (vs. SIO scale)	

rule of thumb: internal reproducibility goals is one half the network compatibility goals



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

Typical plumbing design for CO2 observations

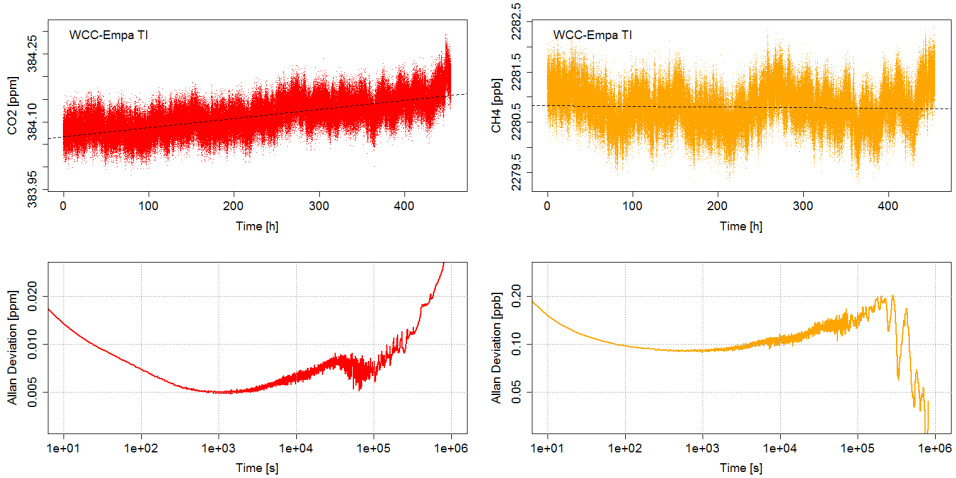


ICOS Atmospheric Station Specification Document
https://www.icos-ri.eu/documents/ATC%20Public

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

Calibration frequency for CO2 observations

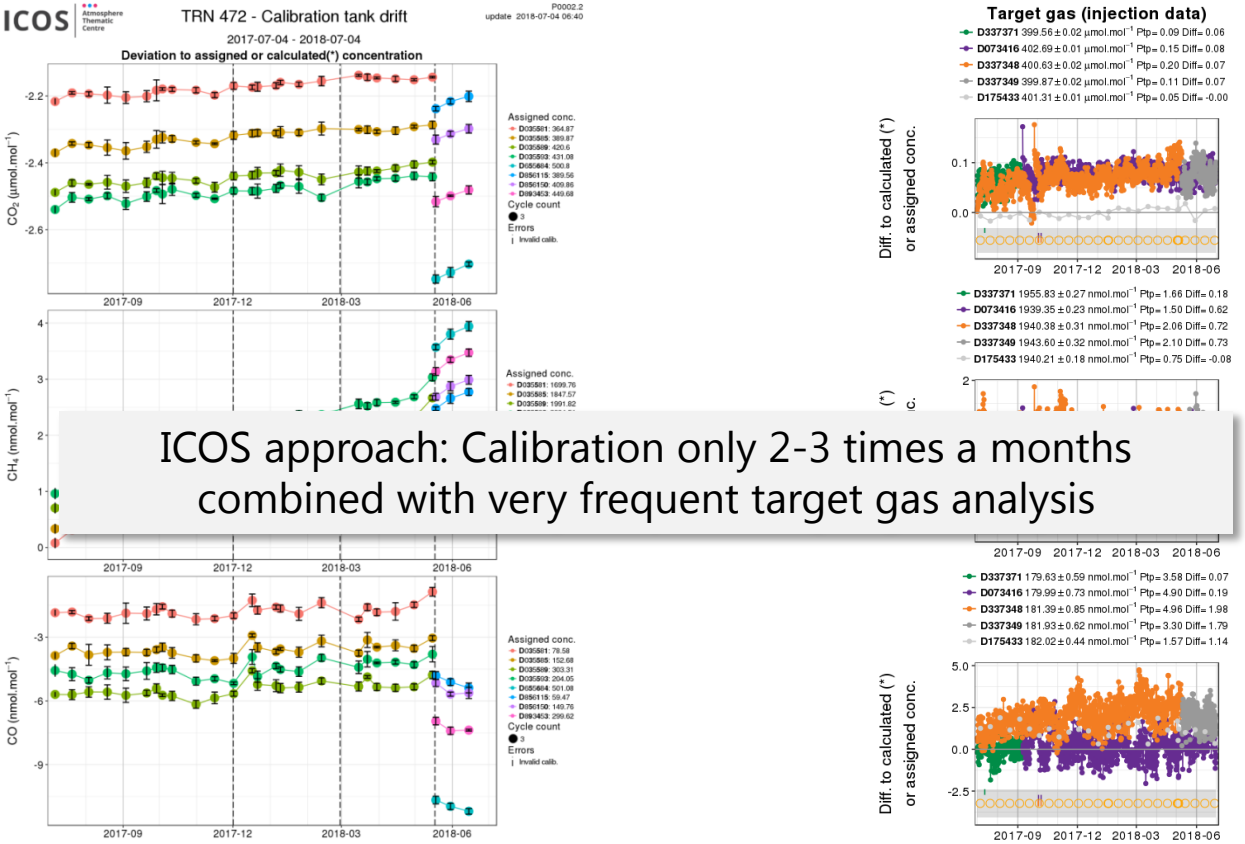
Allan deviation plots



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."

Calibration frequency for CO2 observations

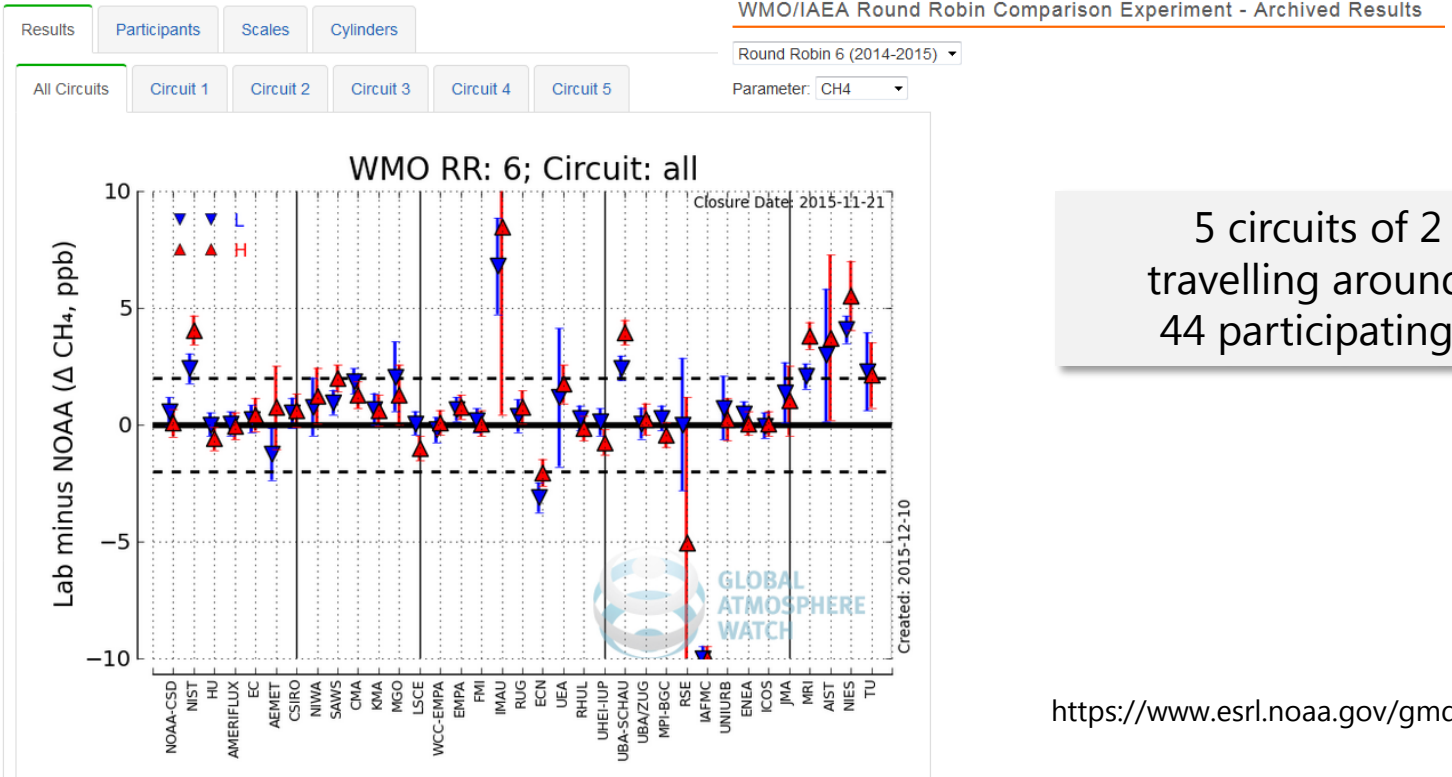


ICOS approach: Calibration only 2-3 times a months combined with very frequent target gas analysis

ICOS ATC (Atmospheric Thematic Center), screenshots

Network wide quality control

- Round Robin Exercises for Greenhouse Gases

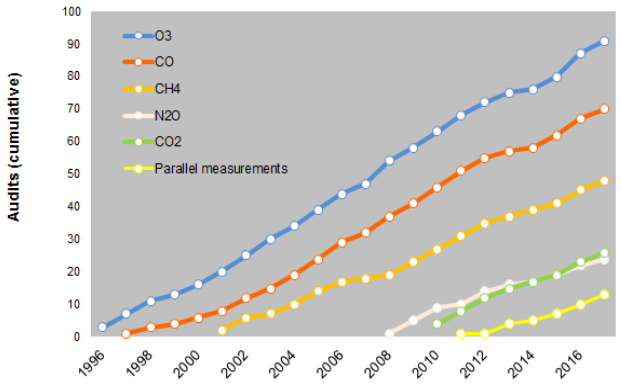


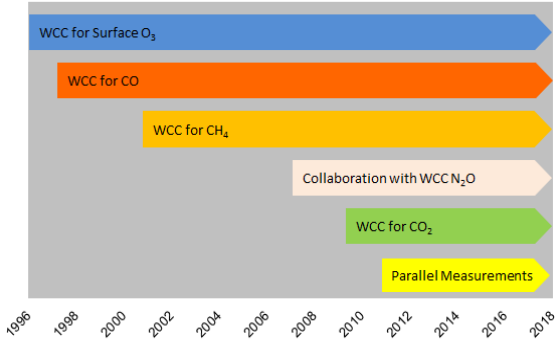
5 circuits of 2 cylinders travelling around the world; 44 participating labs (RR6)

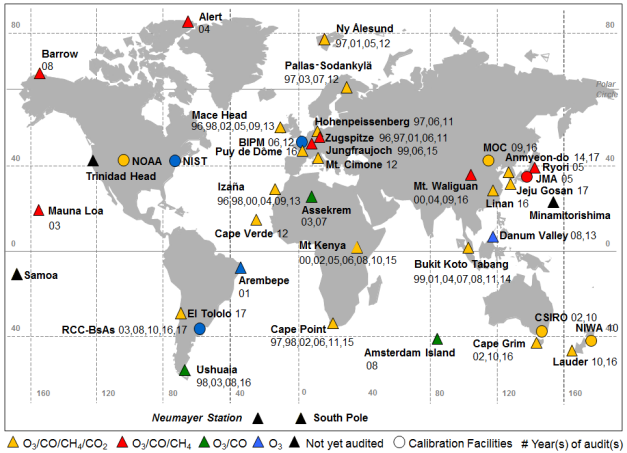
https://www.esrl.noaa.gov/gmd/ccgg/wmorr/

Network wide quality control

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



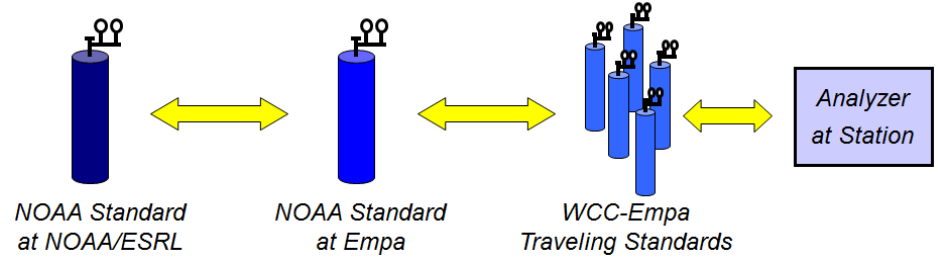


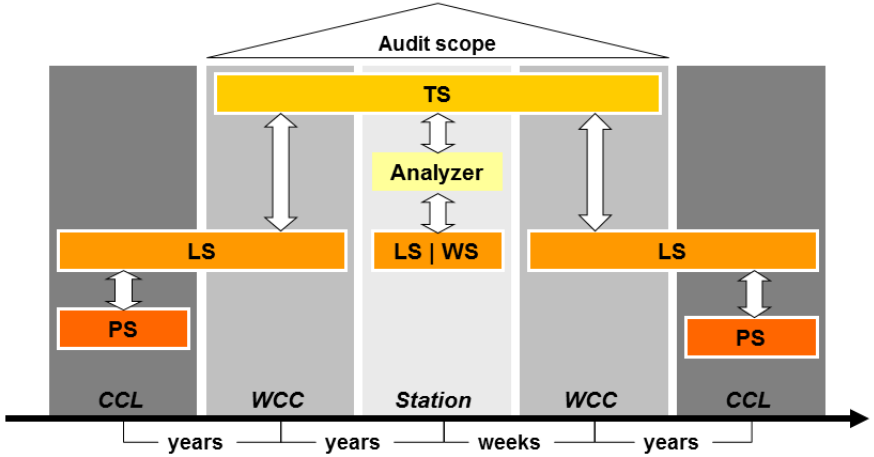


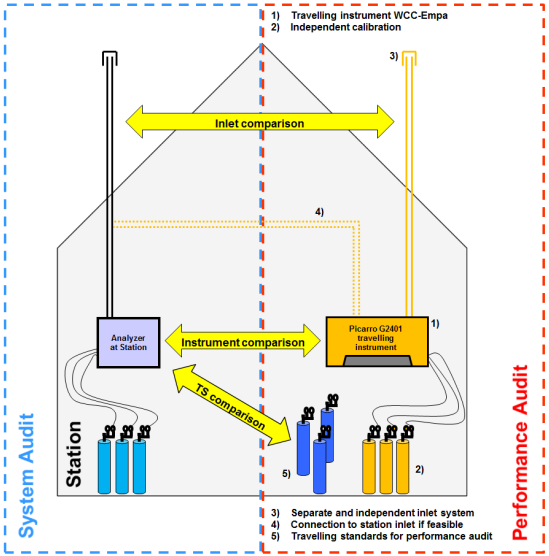
- established in 1996, more than 90 audits since then
- ensures traceability to the GAW reference and determines compatibility
- assists stations with regards to instruments and measurement issues (WCC-Empa & QA/SAC-CH)
- improves technical know-how at stations through on-site training (WCC-Empa & QA/SAC-CH)

Network wide quality control

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



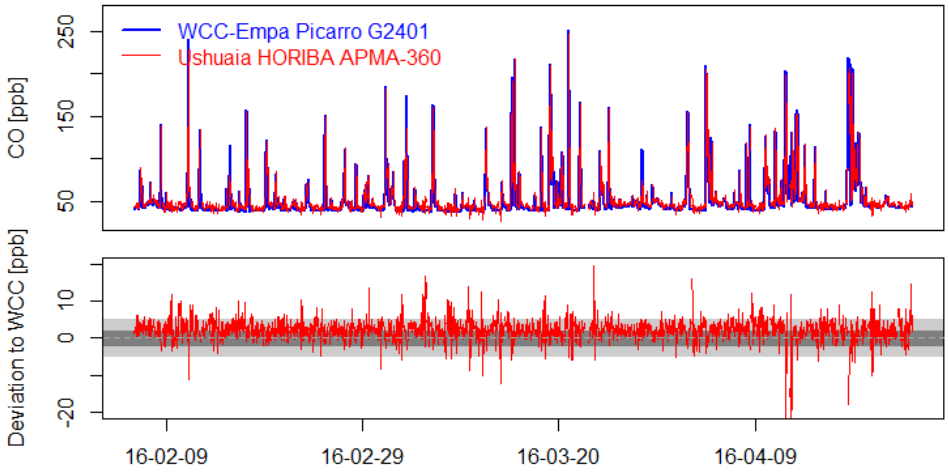




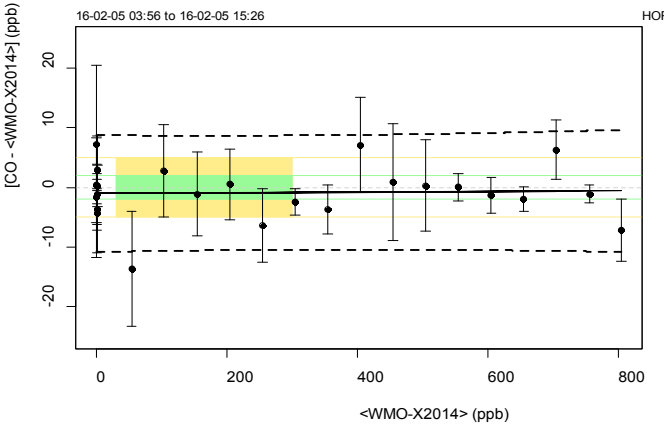
https://www.empa.ch/web/s503/wcc-empa

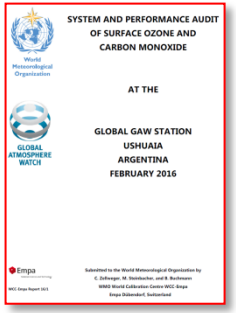
Network wide quality control

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



WCC-Empa audit in Ushuaia (Argentina) (February 2016)




SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE AND CARBON MONOXIDE

AT THE

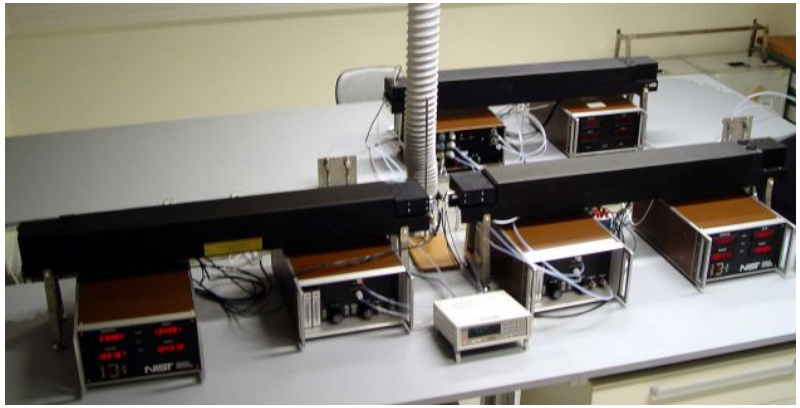
GLOBAL GAW STATION
USHUAIA
ARGENTINA
FEBRUARY 2016

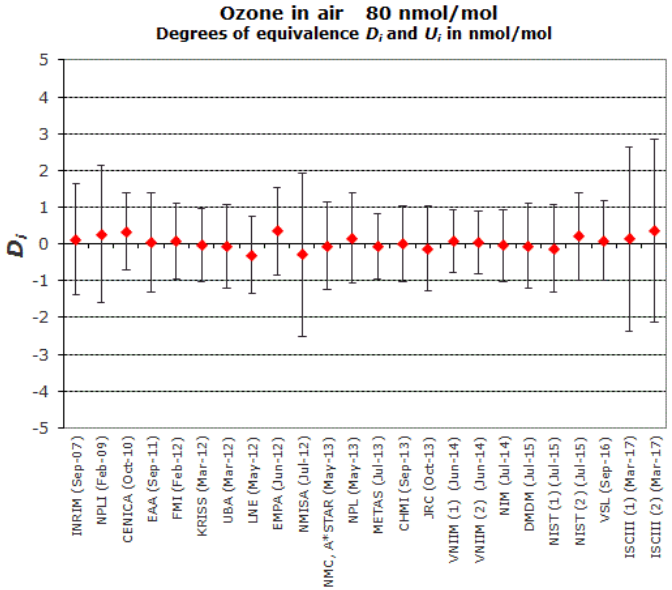
Audit reports are publicly available at

- 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

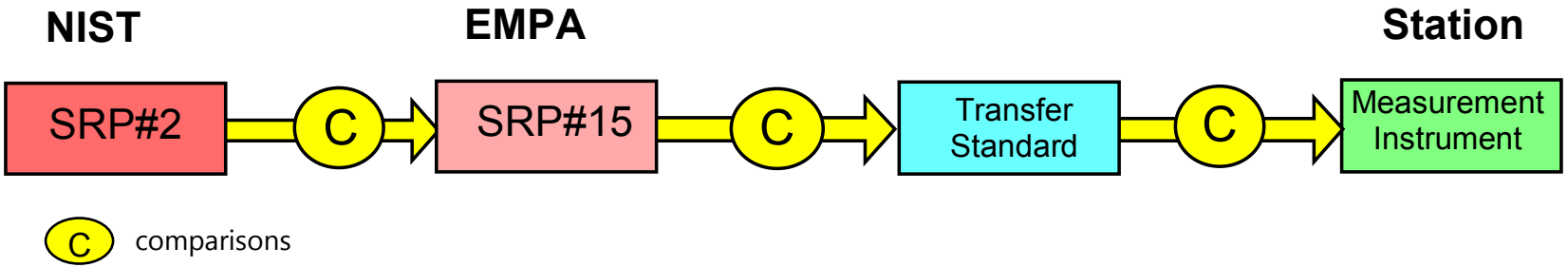
Reference: Standard Reference Photometer (SRP)

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	$0.0014 \cdot x$

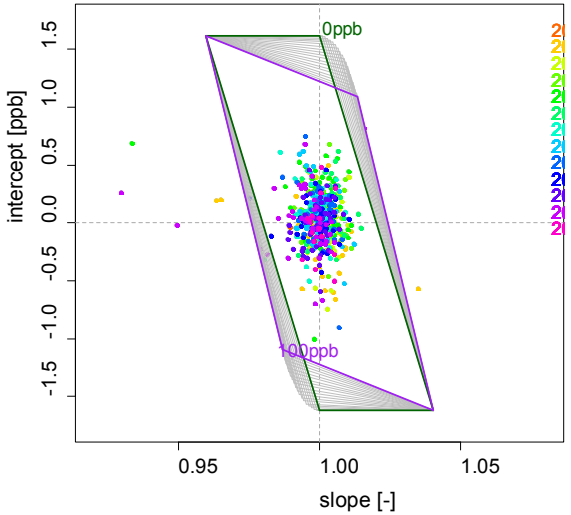
* *where x refers to ozone mole fraction*

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).

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

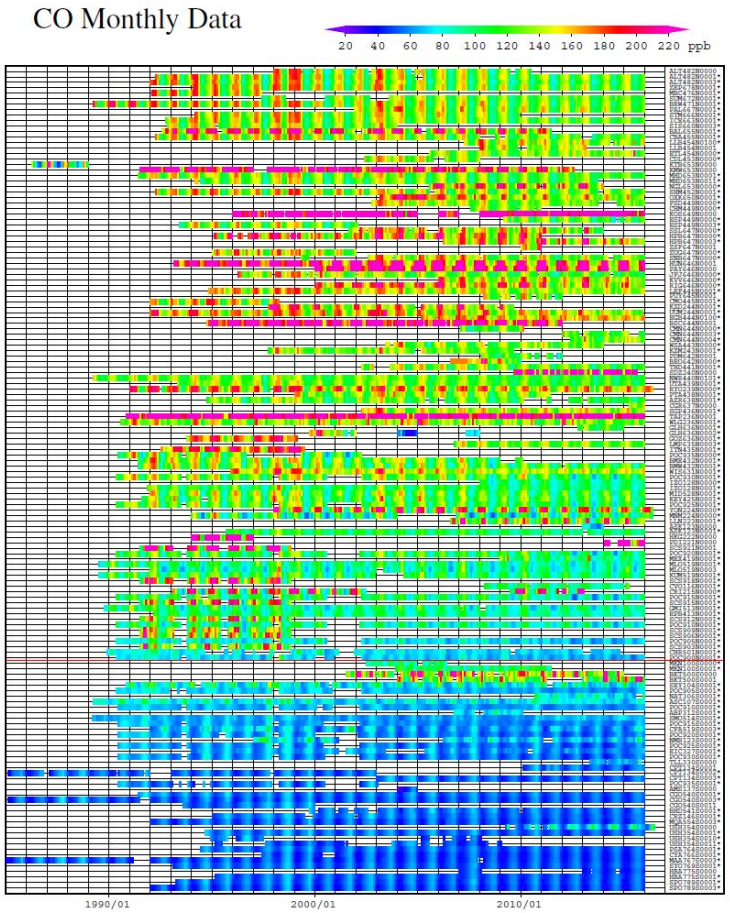
O3 measurement guidelines, GAW Report Nr. 209, 2013

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.

Comparison with other measurements



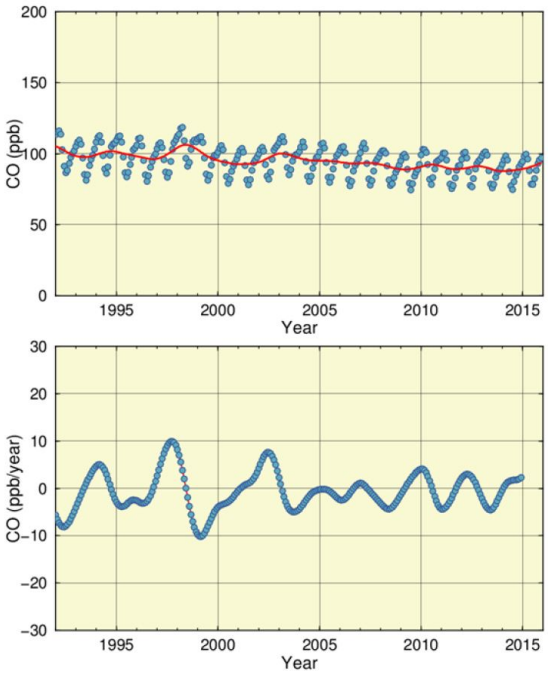
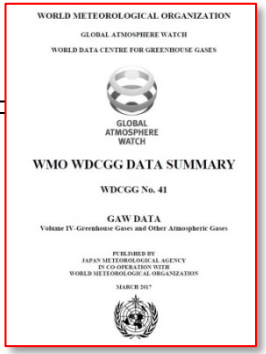


Fig. 7.1 Globally averaged monthly mean mole fraction of CO from 1992 to 2015 and the deseasonalized long-term trend in red line (top), and annual growth rate (bottom).


WORLD METEOROLOGICAL ORGANIZATION

GLOBAL ATMOSPHERE WATCH

WORLD DATA CENTRE FOR GREENHOUSE GASES

GLOBAL ATMOSPHERE WATCH

WMO WDCGG DATA SUMMARY

WDCGG No. 41

GAW DATA

Volume IV-Greenhouse Gases and Other Atmospheric Gases

PUBLISHED BY
JAPAN METEOROLOGICAL AGENCY
IN CO-OPERATION WITH
WORLD METEOROLOGICAL ORGANIZATION

MARCH 2017

source: WDCGG Data Summary 41, 2017
https://gaw.kishou.go.jp/

Comparison with other measurements

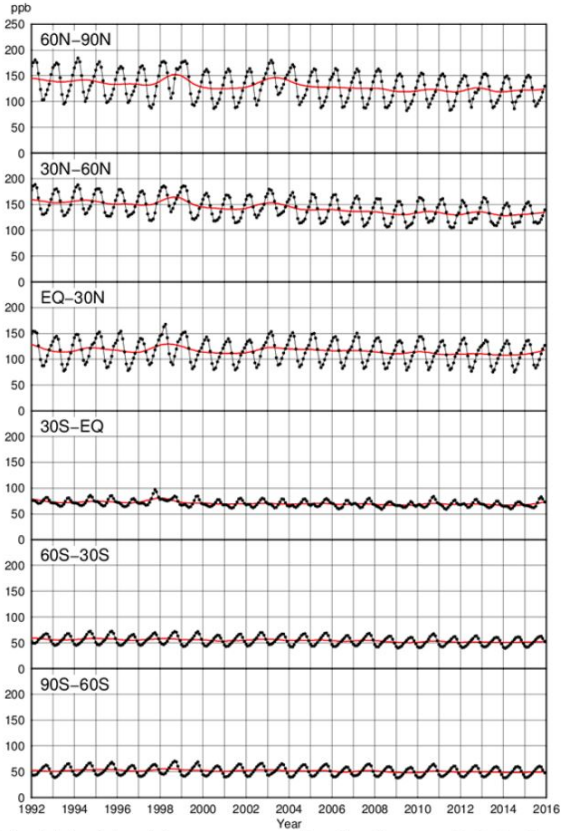


Fig. 7.2 Monthly mean mole fractions of CO from 1992 to 2015 for each 30° latitudinal zone (dots) and their deseasonalized long-term trends (red lines).

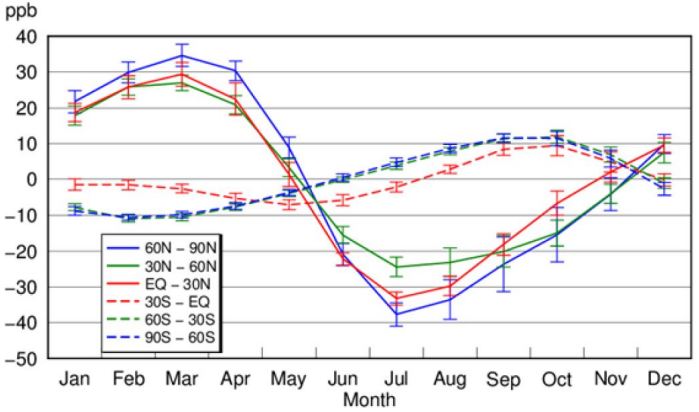
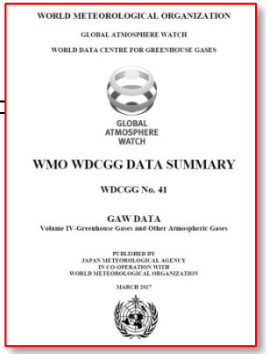
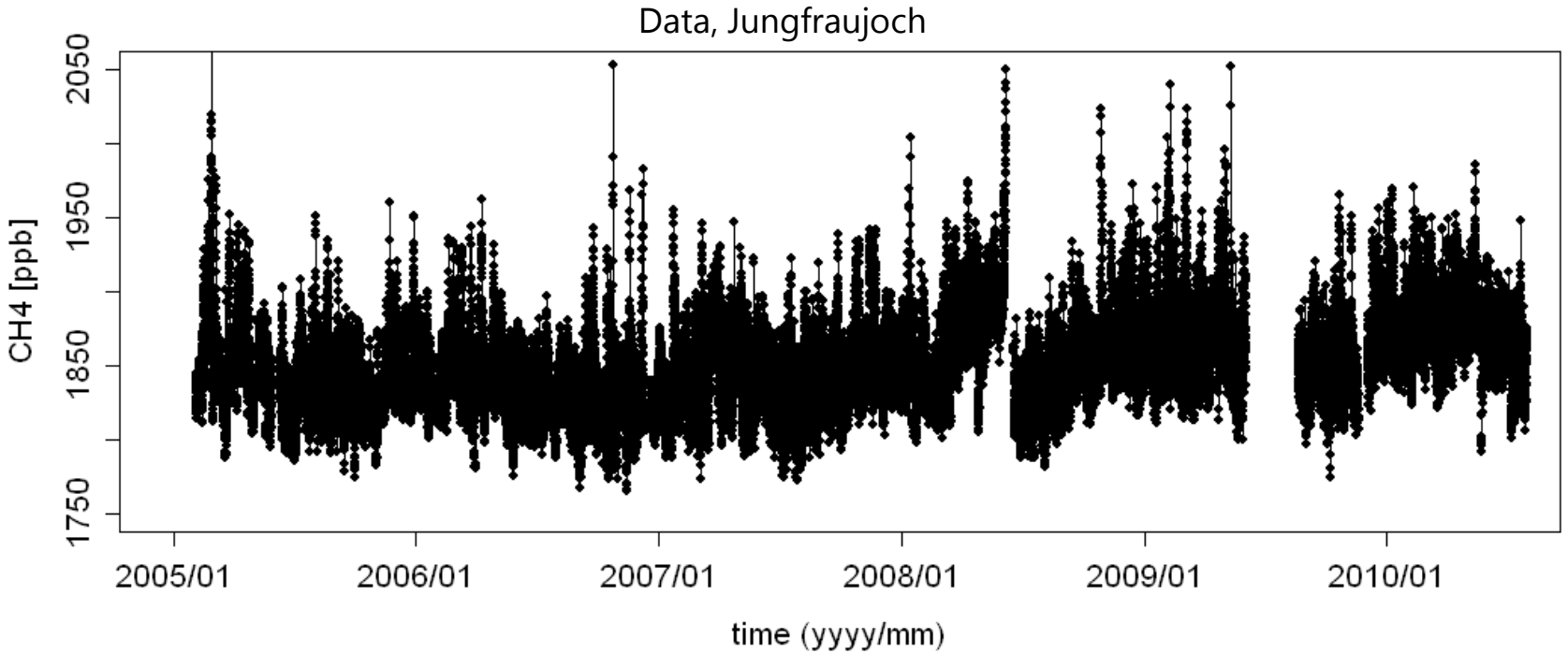


Fig. 7.4 Average seasonal cycles of CO mole fractions for each 30° latitudinal zone obtained by subtracting long-term trends from the zonal mean time series. Error bars represent the range of ±1σ calculated for each month. (period 1992 to 2015).

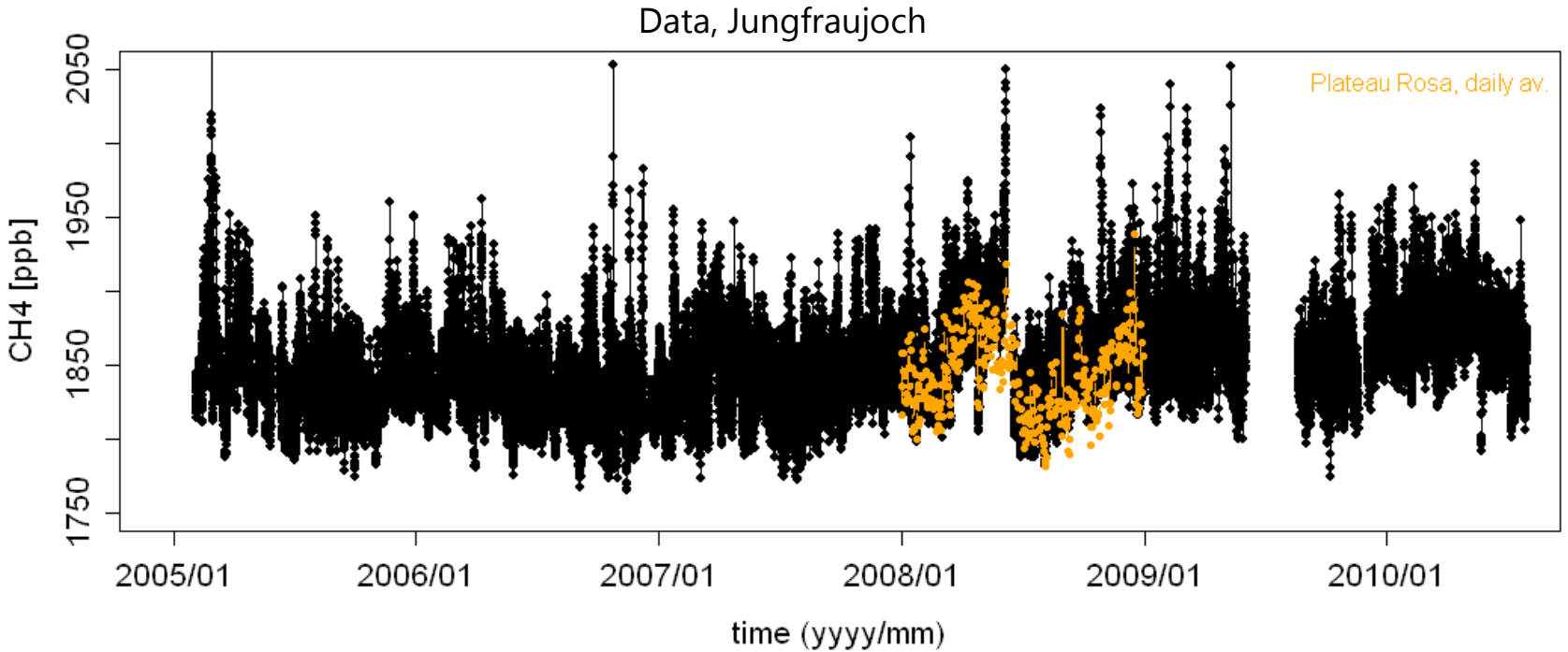


source: WDCGG Data Summary 41, 2017
https://gaw.kishou.go.jp/

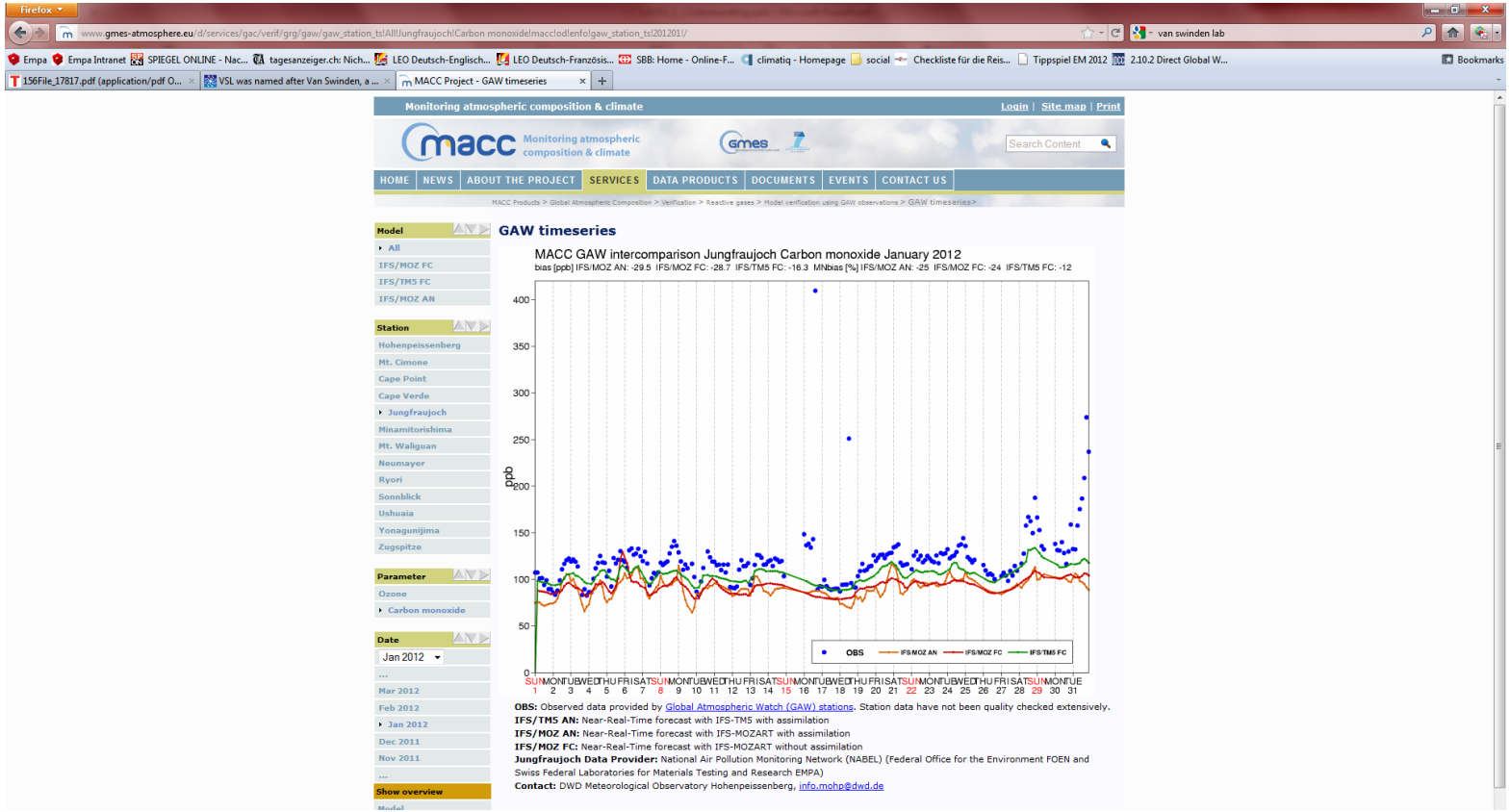
Comparison with other measurements



Comparison with other measurements



Comparison with and use of models



SAMLAC, Puerto Rico, 12 November 2018

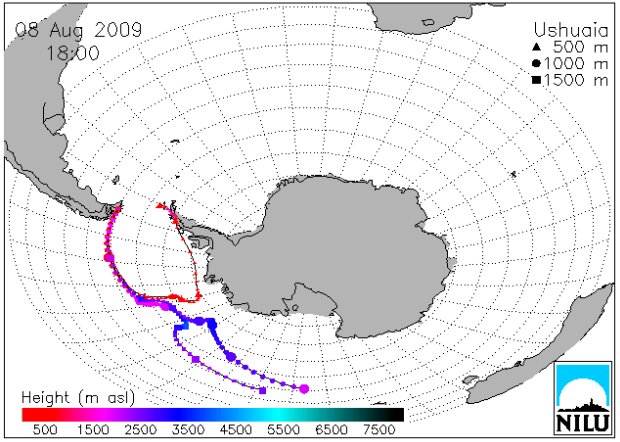
Comparison with and use of models

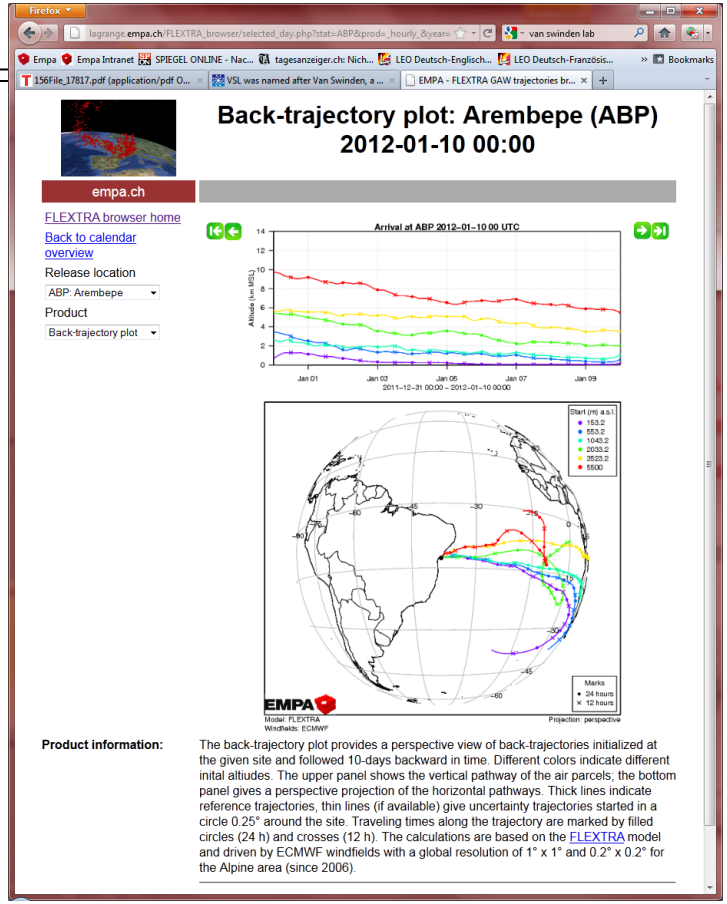
Available through the internet from various sources

http://lagrange.empa.ch/FLEXTRA_browser/

http://www.emep.int/trajectories.html

http://www.arl.noaa.gov/ready/hysplit4.html





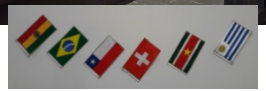
Training Opportunities

V Intercomparación de Analizadores de Ozono Superficial

CRC III - WMO

Buenos Aires - Argentina

23 – 27, Octubre, 2017



SAMLAC, Puerto Rico, 12 November 2018

Training Opportunities

Locación: IIDEPROC; La Paz, Bolivia

Hora	Lunes	Martes	Miércoles	Jueves	Viernes
08:00-10:00		**Aerosoles** SOP; peso de filtros en atmosfera estándar; interpretación	**Gases raros** Medida continuo de ozono, NO_x, CO y SO_2; ventaja/desventajas de diferentes técnicas de medición	**Análisis y filtración de datos** Flujo de datos; automatización;	**Discusión** Discusión general de problemas frecuentes con las medidas en la Red MoniCA
10:00-10:30		Descanso	Descanso	Descanso	Descanso
10:30-12:30		**Aerosoles** SOP; peso de filtros en atmosfera estándar; interpretación	**Gases raros** ventaja/desventajas de diferentes técnicas de medición	**Análisis y filtración de datos** Filtración de datos; ventaja/desventaja de diferentes softwares	**Repaso** Puntos principales
12:30-14:00	Almuerzo-bocadillo con llegada; bienvenida y presentación de los participantes	Almuerzo	Almuerzo	Almuerzo	Almuerzo
14:00-16:00	**Ley, Razón, Salud**: Porque tenemos que hacer medidas	**Visita del IIDEPROC** Práctica en las temas de calibración y manutención de los aparatos	**Gases raros (*)** Calibración; Estándar de gases de calibración; jerarquía de gases de calibración	**Análisis y filtración de datos (*)** Filtración de datos; automatización y labor manual	**Excursión estación GAW Chacaltaya** Partida ~ 13:30 Llegada ~19:00
16:00-16:30	Descanso		Descanso	Descanso	
16:30-19:00	**Medidas con el método pasiva** Intercomparación activa/pasiva; Procedimientos operativos estándar (SOP); Análisis		**Gases raros (*)** Manipulación de botellas de gas de calibración	**Análisis y filtración de datos (*)** Visualización;	

(*) Con ejercicios

airelimpio

October 2015

Capacitación de CATCOS a la red MoniCA

Curso de formación sobre Monitoreo de la calidad del aire urbano en Bolivia

J. G. Anet, M. Steinbacher

Foto: Archivo Aire Limpio

Técnicos de la Red MoniCA capacitados por el EMPA.

Recientemente, se llevó a cabo el Curso de formación sobre Monitoreo de la calidad del aire urbano en Bolivia, para técnicos de la Red MoniCA (Red de Monitoreo de Calidad de Aire), en la ciudad de La Paz, del 12 octubre al 16 octubre. El curso tuvo como objetivo fundamental mejorar la comprensión y fomentar el conocimiento de los técnicos que trabajan día a día para la Red MoniCA Bolivia, estuvo a cargo de dos expertos en medición de calidad del aire, del Laboratorio Suizo Federal de Ciencia de los Materiales y Tecnología (EMPA).

El curso fue organizado dentro del Programa Fomento de Actividades y Coordinación dentro de la Red MoniCA. Se inició con una introducción con los ajustes de las medidas en Bolivia, en un contexto más amplio, se prosiguió con el marco legal, los efectos adversos de la contaminación atmosférica en la salud del hombre y los ecosistemas, como así también la definición de los límites de calidad del aire. También, se realizaron presentaciones y discusiones de las técnicas de medición de muestras pasivas, técnicas de medición activas y continúas más avanzadas para los aerosoles y los gases.

Se instruyó a los técnicos en el manejo de una herramienta computacional de procesamiento de datos que realiza un primer

traducción simultánea del inglés al español. A pesar de este inconveniente, a menudo, las sesiones terminaron en discusiones animadas y no en largas charlas de los ponentes. Muchos participantes compartieron temas específicos de sus estaciones con el fin de discutirlos en la sesión plenaria, haciendo el curso aún más beneficioso para todos. Además los momentos de descanso y el almuerzo fueron ampliamente utilizados para continuar la discusión específica en grupos más pequeños.

Durante los debates, se identificaron algunas deficiencias en la Red MoniCA y se desarrollaron estrategias para superar estas deficiencias en el futuro. Se prestará especial atención a la reformulación y la aplicación de los procedimientos de operación estándar. La falta de una infraestructura adecuada como ser; una fuente fiable de alimentación eléctrica o la conexión a Internet en algunas estaciones de medición, deben ser objeto de mejora en el futuro.

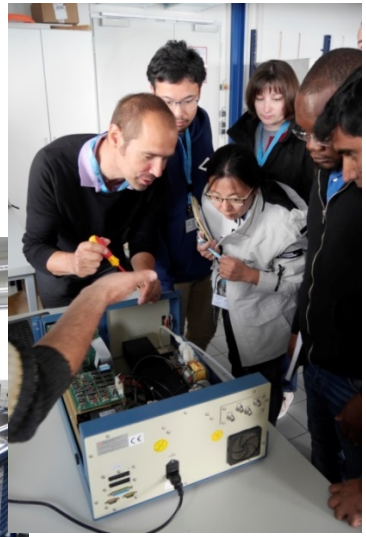
Conclusiones

El Curso de formación sobre Monitoreo de la calidad del aire urbano en Bolivia fue muy exitoso, se logró desnudar ciertas falencias técnicas, fortalecer los conocimientos existentes y promover nuevas habilidades del personal de Red MoniCA. Aunque el curso fue relativamente corto, la retroalimenta-

Training Opportunities

https://www.gawtec.de/

two courses per year



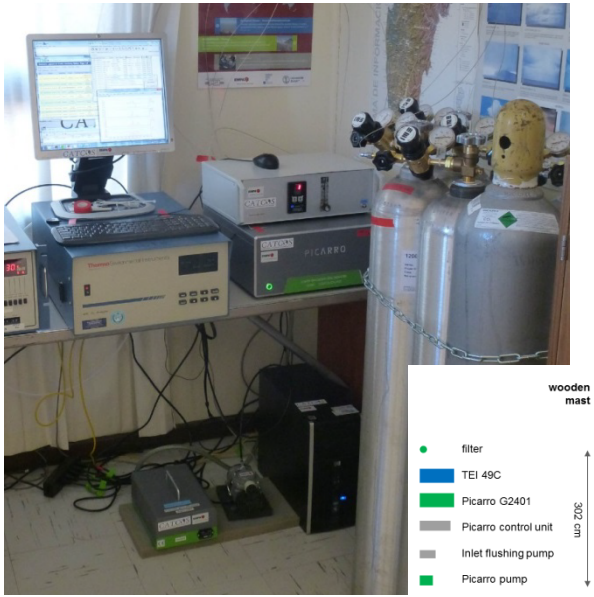
Implementation of new measurements in South America

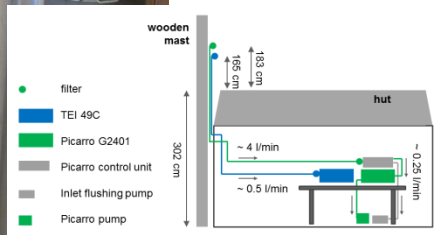
in April 2013, measurements are still ongoing

measurement station

inlet

installed equipment





CATCOS
Capacity Building and Twinning for Climate Observing Systems

Implementation of new measurements in South America

in April 2013, measurements are still ongoing

measurement station

inlet

Data acquisition and logbook

CATCOS
Capacity Building and Twinning for Climate Observing Systems

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
- A wide range of data from observations and models are available online
  - make use of it !
  - profit from training opportunities and potential collaborations

Station setup and operation