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GAW

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Quality control supporting climate policy and research: Assessing two decades of GAW audit results for N_2O and CO

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EGU
Photography encouraged

Supporting climate policy and research

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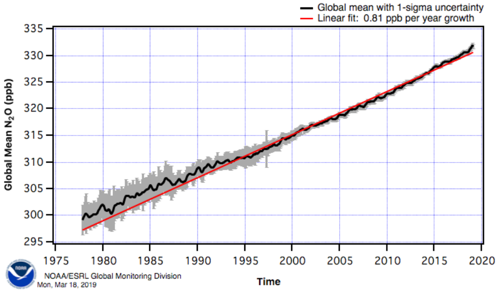
- Need for reliable / traceable data

Well-established integrated global observations are essential for understanding the global carbon cycle and the role of greenhouse in climate change.



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

- Global Atmosphere Watch (GAW)

Currently GAW coordinates activities and data from 31 global stations, more than 400 regional stations, and around 100 contributing stations.

http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html

- GAW QA/QC framework

Measurements must be expressed in the same units and on the same scale and data from different countries and from different sites are must be comparable.

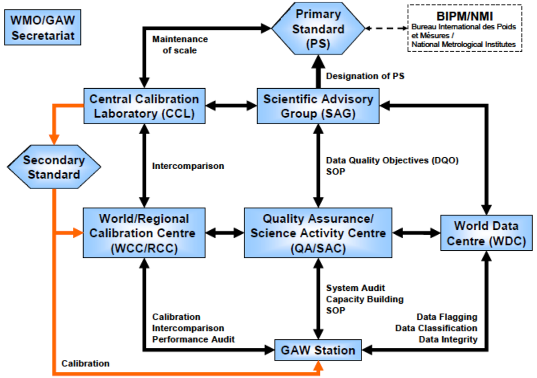


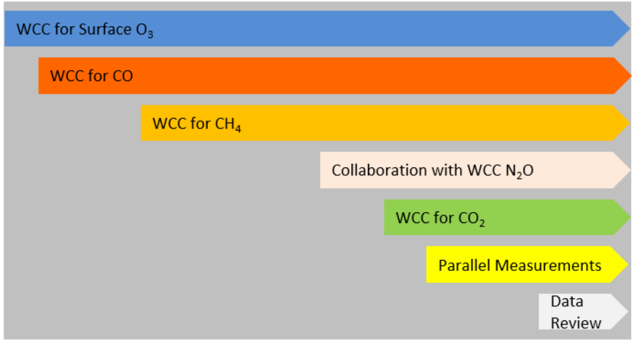
Figure 15 - Elements of the Quality Assurance system, QA activities and workflow in GAW

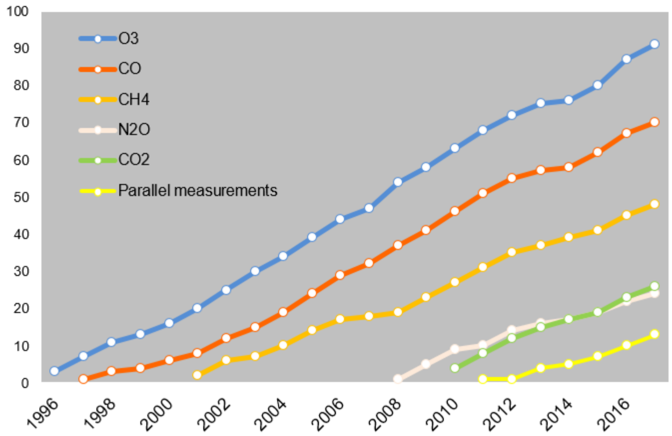
GAW Implementation Plan for 2016-2023

World Calibration Centre WCC-Empa

- Supports global research and policies since 1996
- More than 90 station audits at mainly global GAW stations
- Covers four important greenhouse and reactive gases
- Collaborates with other calibration centres to improve traceability
- Assesses the performance of stations also with parallel measurements
- Audit procedure includes data and metadata review

Audited stations by WCC-Empa since 1996 (red triangles); multiple audits at many stations





Scope (top) and cumulative number (bottom) of WCC-Empa audits

Audits: Travelling Standards vs. Parallel Measurements

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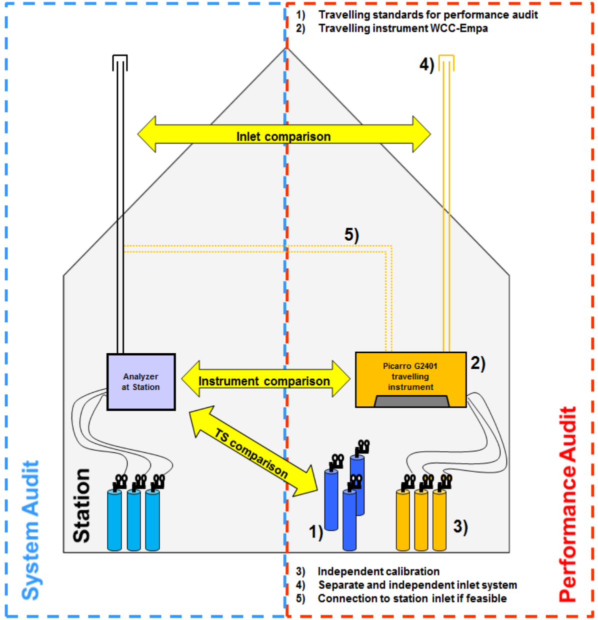


- ☹ Only instrument comparison
- ☹ Snapshot in time
- ☹ Special care might influence results
- ☺ Covers wider mole fraction range
- ☺ Repeatability conditions

- ☺ Assessment of the whole system
- ☺ Longer time period
- ☺ Less influence by operator
- ☹ Limited to ambient mole fraction range

Instrument development (example for CO)

GC/HgO @ MLO

NDIR @ ASK

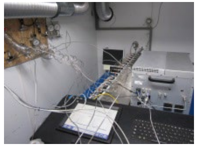
VURF @ CVO

GC/FID/ECD @ PAL

+CH_4, SF_6, N_2O

FTIR @ LAU

+N_2O CH_4, CO_2, $\delta^{13}C$



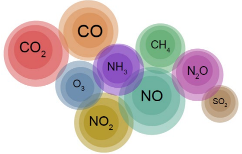
OA-ICOS @ CVO +N_2O

CRDS @ AMY

+CH_4, CO_2

Mid-infrared (MIR) direct laser absorption spectroscopy

1990 2000 2010 2019



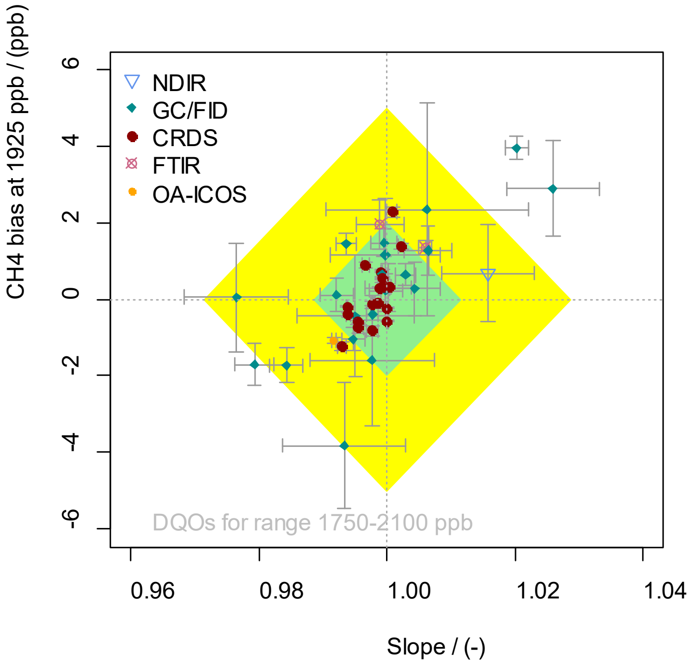
Trend:

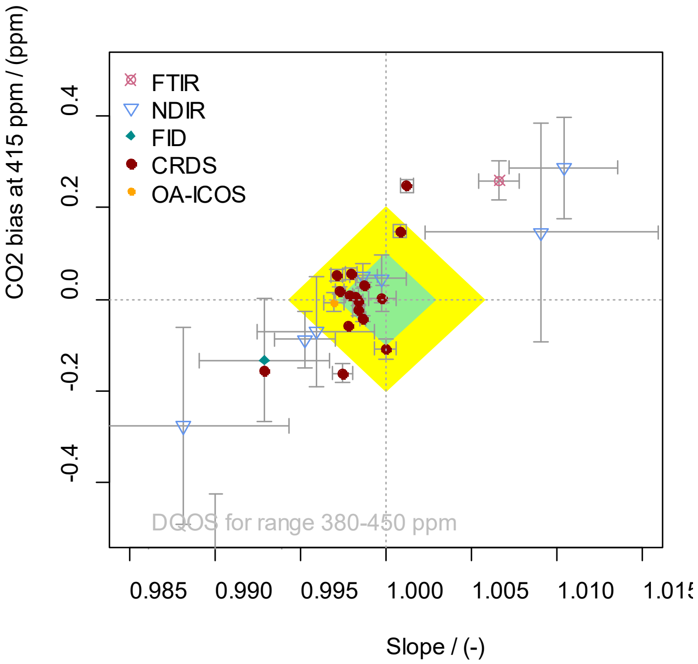
- Slow to fast
- Quasi continuous to continuous
- Single- to multi-species

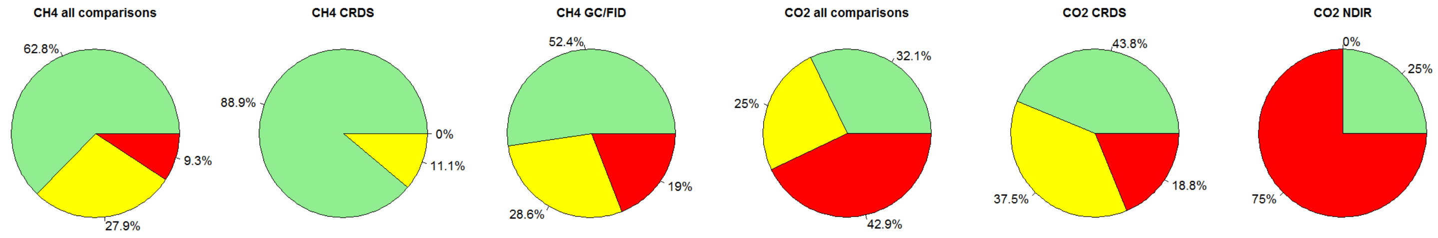
- Measurement of one parameter
- Often slow, quasi continuous
- Frequent calibrations necessary
- Partly non-linear response
- Noise and reproducibility poor compared to current techniques

- Detection of multiple species
- Fast, continuous
- Required calibration frequency varies
- Often linear over a large range
- Improved noise and reproducibility

Results of methane and carbon dioxide audits

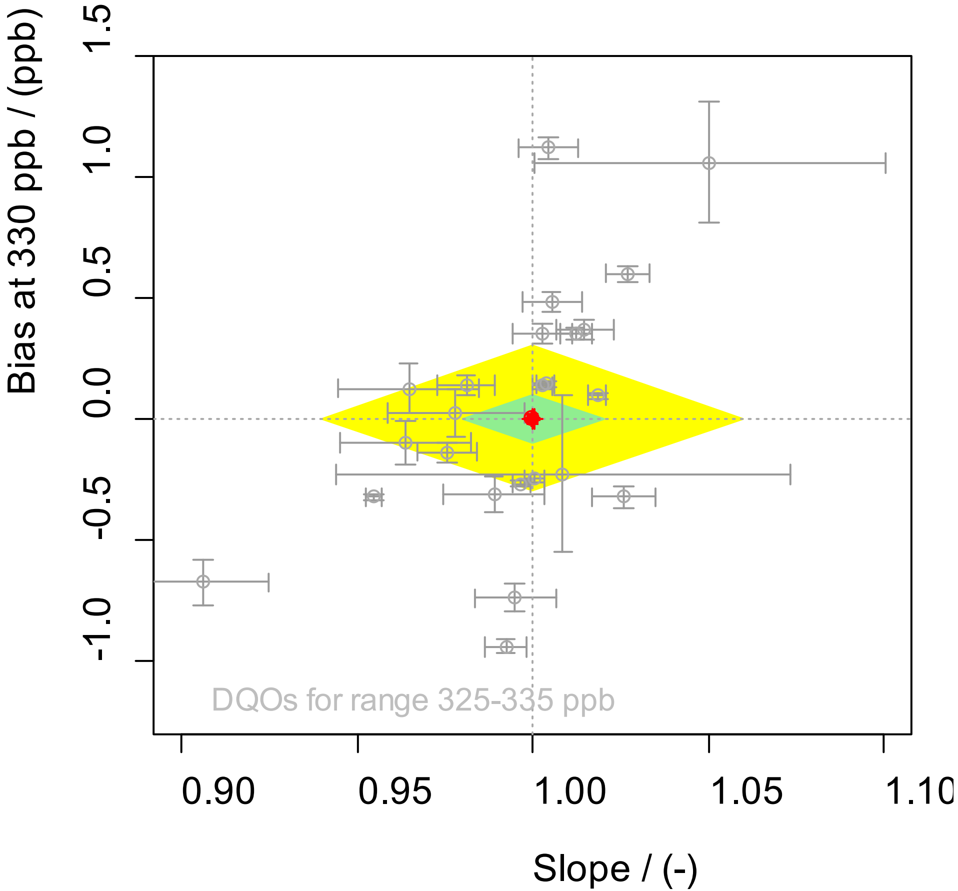




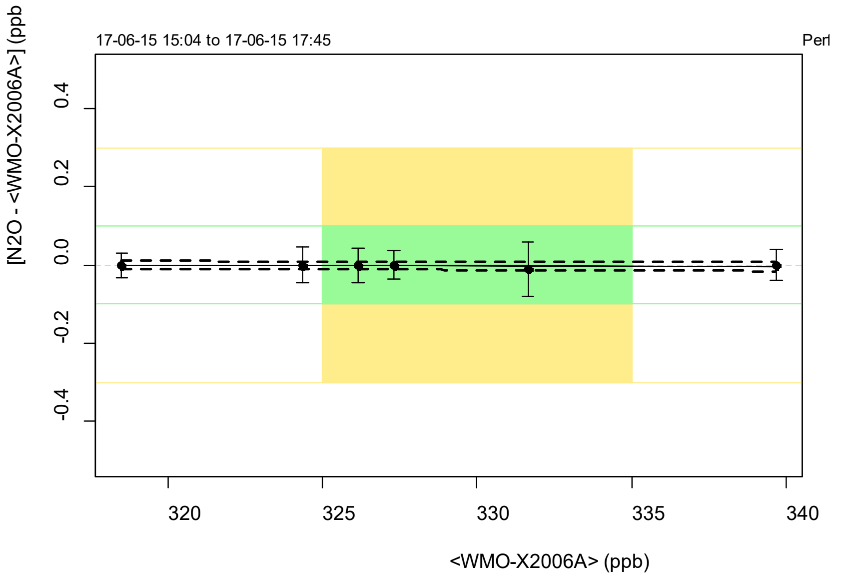


- Update from Zellweger et al. (2016).
- Newer techniques perform better compared to NDIR (CO_2) and GC/FID (CH_4).
- Comparisons shown here are only for
  - analyzers without instrumental problems and
  - calibrations on the same scale

What can we learn from these plots?



- Perfect agreement:
  - No bias at center of relevant mole fraction range
  - Slope = 1



What can we learn from these plots?

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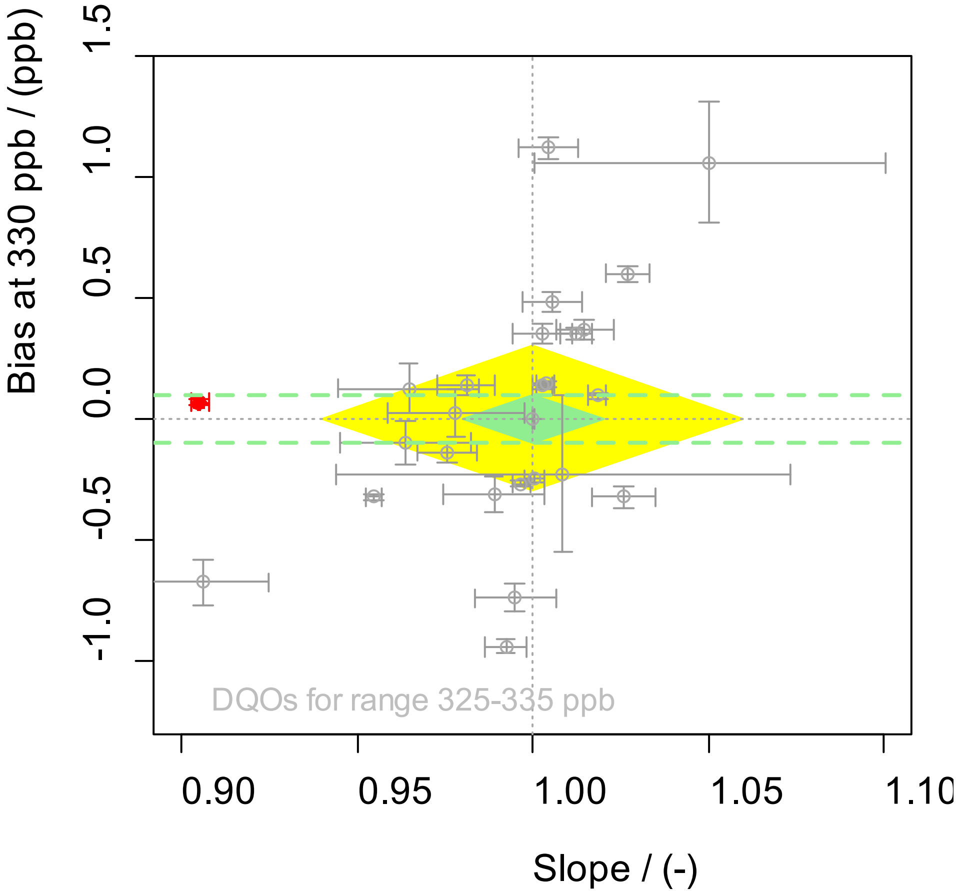
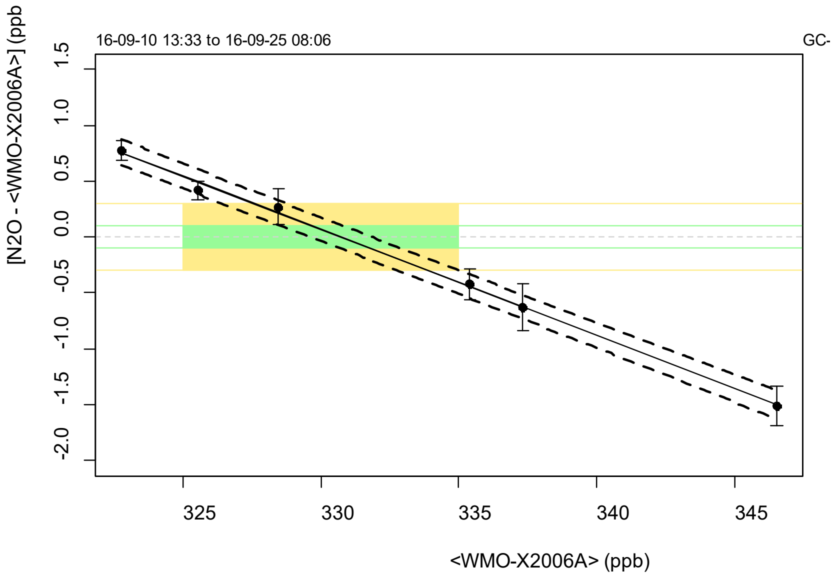


- Good linearity, small bias at relevant level:
  - Small or no bias at center of relevant mole fraction range
  - Slope ≠ 1



What can we learn from these plots?

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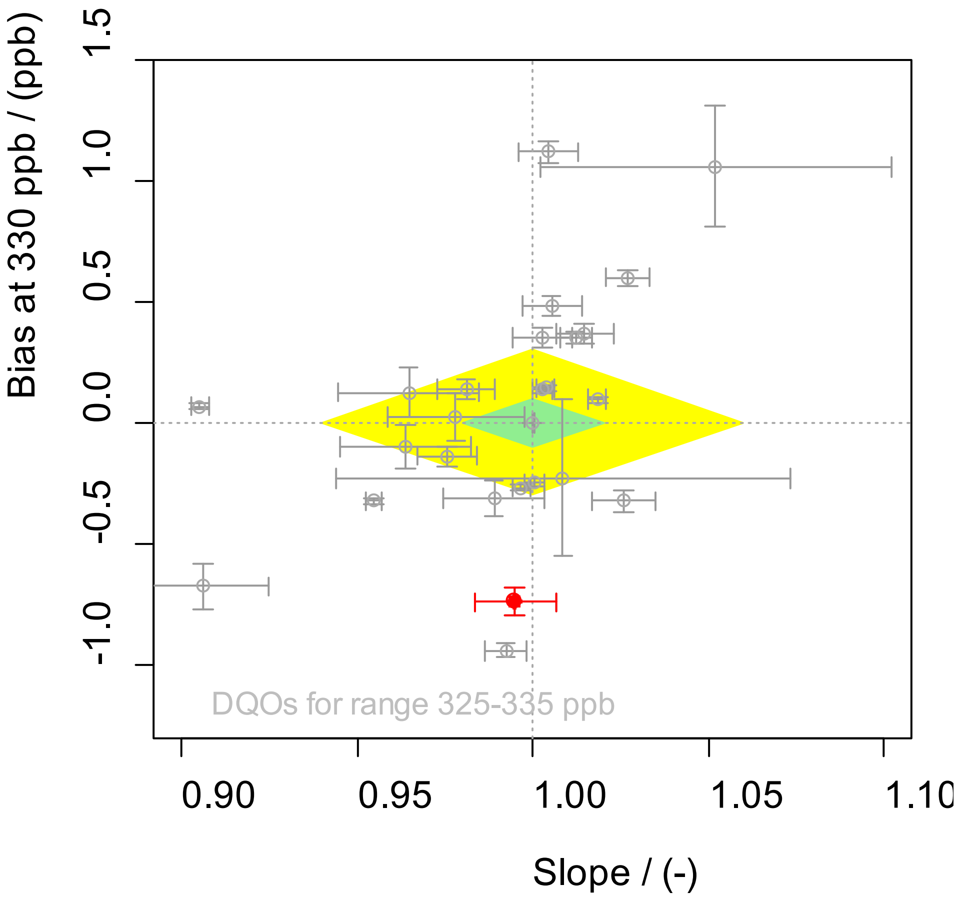
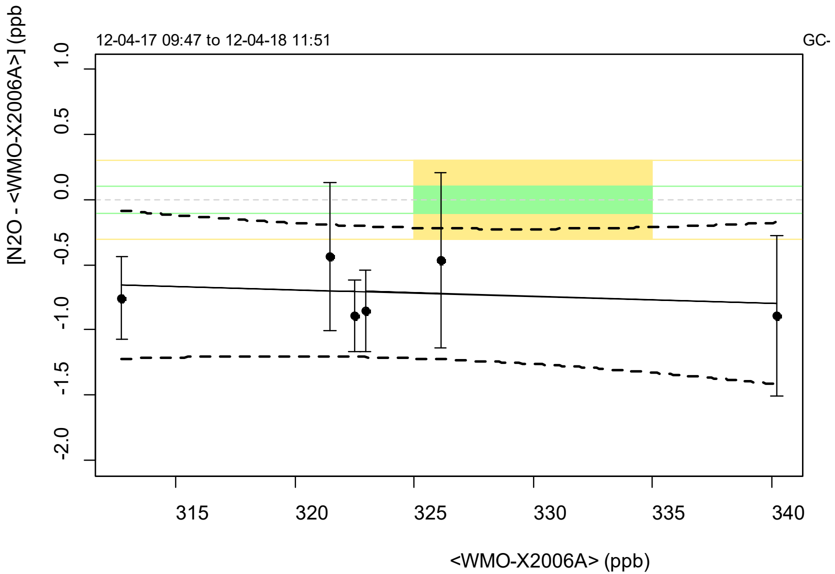
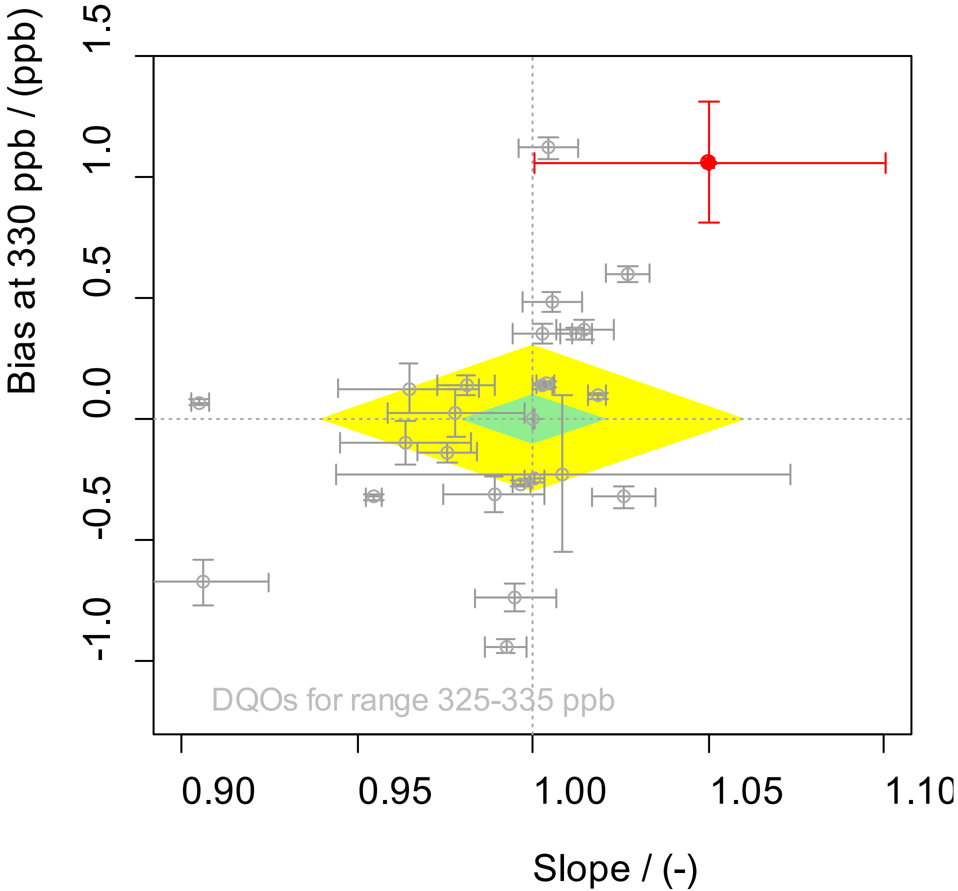


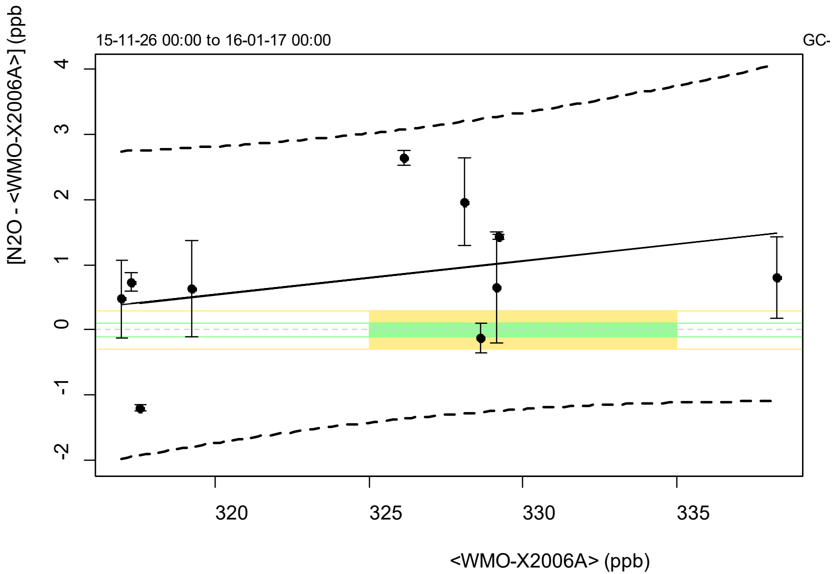
- Offset:
  - Offset at over entire mole fraction range
  - Slope ≈ 1



What can we learn from these plots?

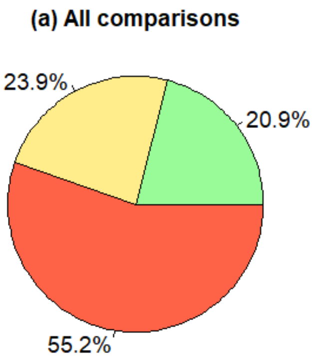


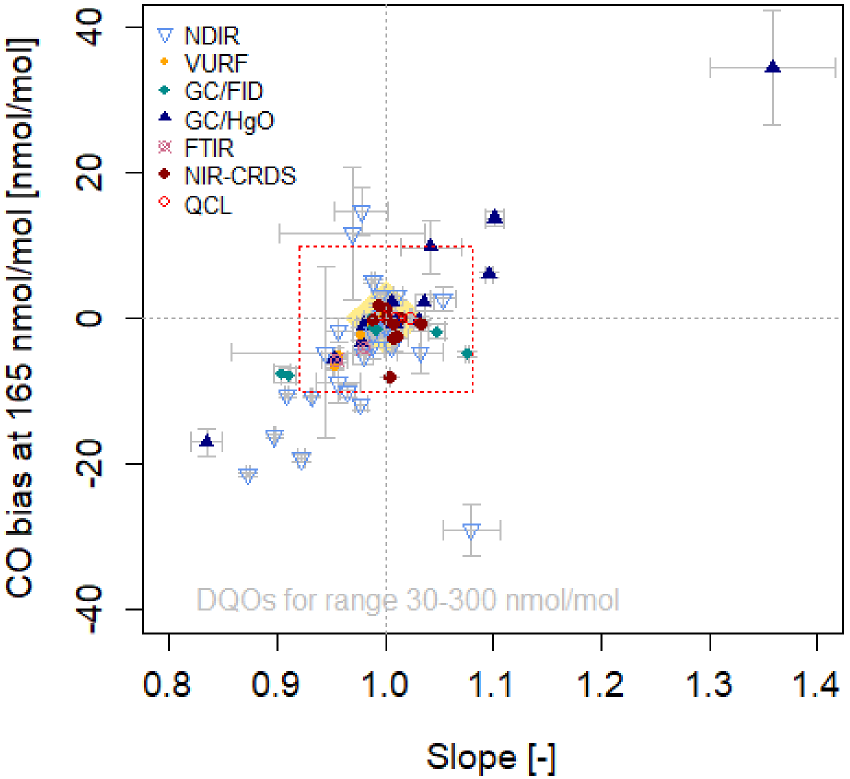
- Poor linearity / scatter:
  - Large uncertainty bars



Results of CO audits

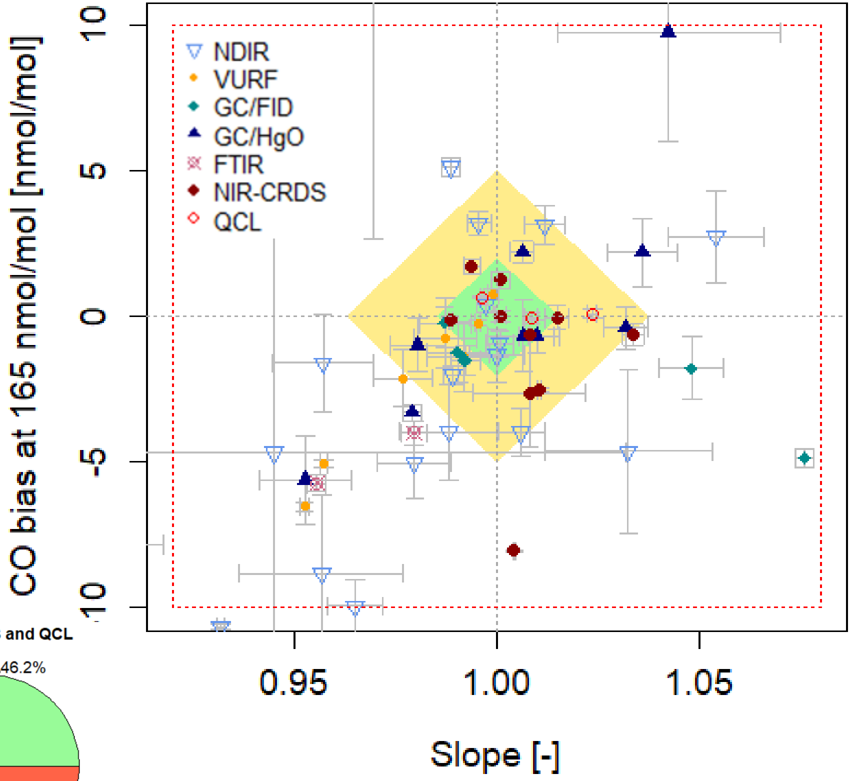
- 67 WCC-Empa audits (2005 – 2019)
- Different measurement techniques
- Data Quality Objectives 2 ppb / 5 ppb
- 21% of the audits met the goal of 2 ppb
- 24% were within 5 ppb
- 55% showed a larger bias (if the range from 30 – 300 ppb is considered)

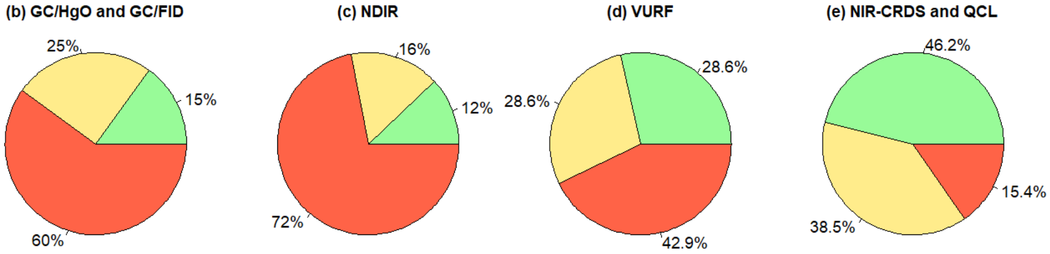




Results of CO audits

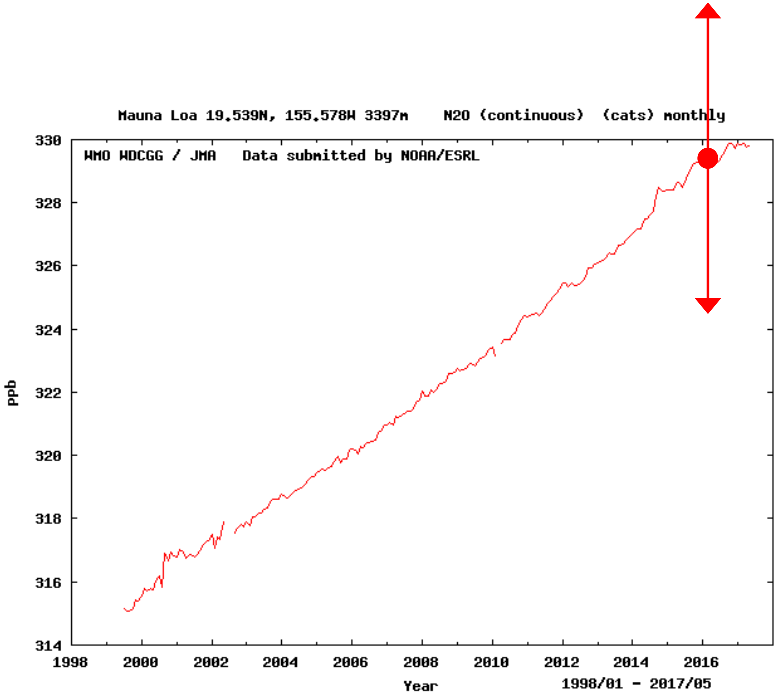
- Large performance difference between different techniques.
- GC systems and NDIR relatively poor, only few were meeting quality goals.
- Better: QCL, CRDS, (VURF)
- But be careful: Standard comparisons have limitations .





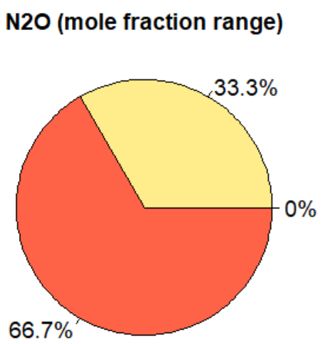
Concept with fixed range problematic for N_2O…

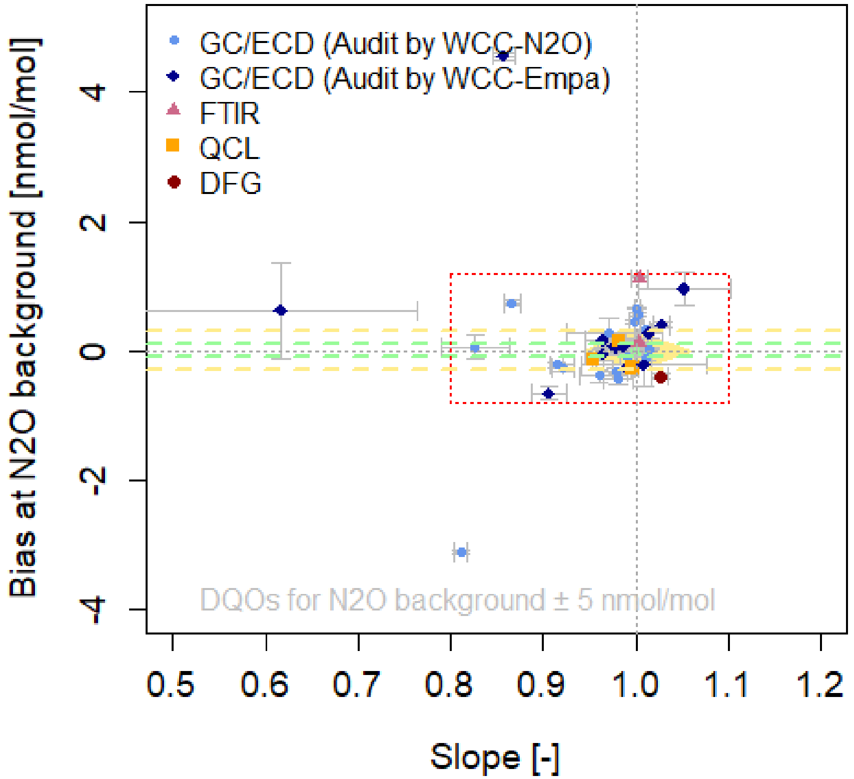
- WCC-N_2O and WCC-Empa audits span almost 20 years (2002 – 2018).
- N_2O shows little variation in ambient air but is growing by 0.8 ppb per year.
- Mean global atmospheric N_2O mole fraction was 328.9 ppb in 2016.
- Stations often ‘focus’ their calibration on ambient levels (GC/ECD is non-linear).
- A range of ± 5 ppb from the global mean of the corresponding year was chosen for the comparison of audit results.
- WCC-N_2O (2001 – 2013) and WCC-Empa (2009 – 2018) audits were analyzed.



Results of N_2O audits

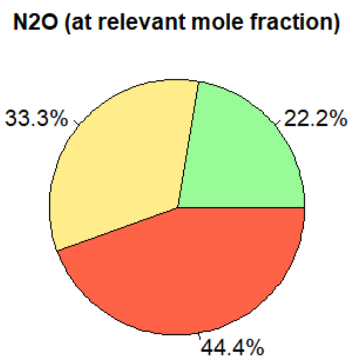
- 20 WCC-Empa audits (2009 – 2018)
- 16 WCC-N_2O audits (2002 – 2013)
- Mostly GC/ECD systems
- Data Quality Objectives 0.1 ppb / 0.3 ppb
- None of the audit met the goal of 0.1 ppb
- One third of the audits was within 0.3 ppb (if a range of 10 ppb is considered)

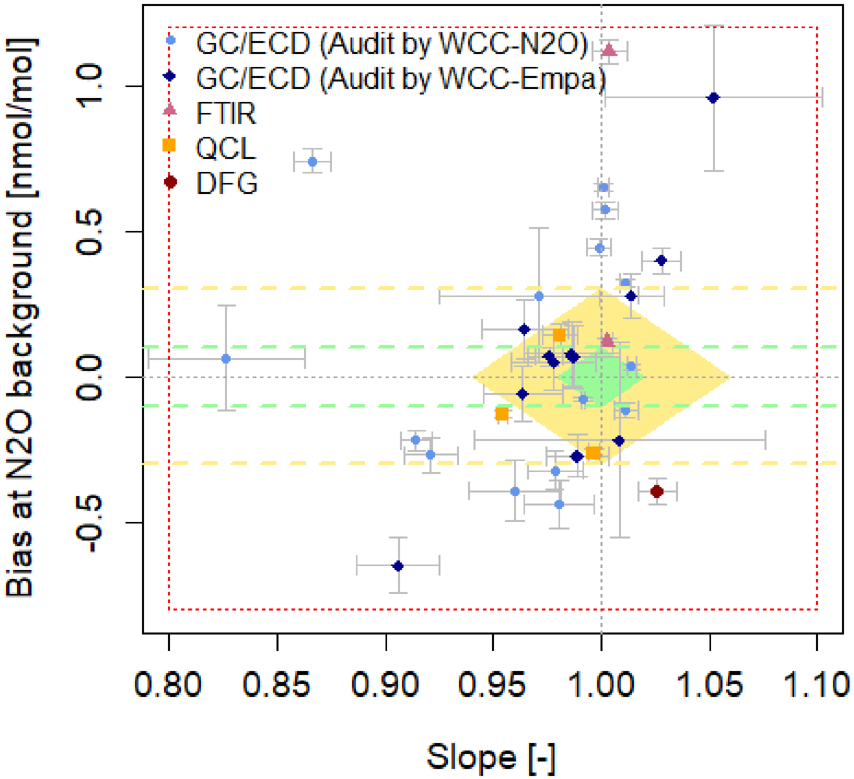




Results of N_2O audits

- No clear advantage of newer techniques, yet too few comparisons
- Uncertainty of bias / slope on average smaller for e.g. QCL systems
- Limiting factor is the uncertainty of the calibration standards





Results of N_2O audits compared to WMO round robin

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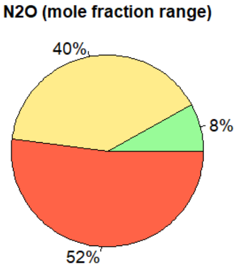
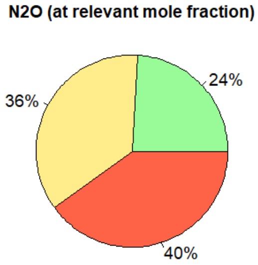
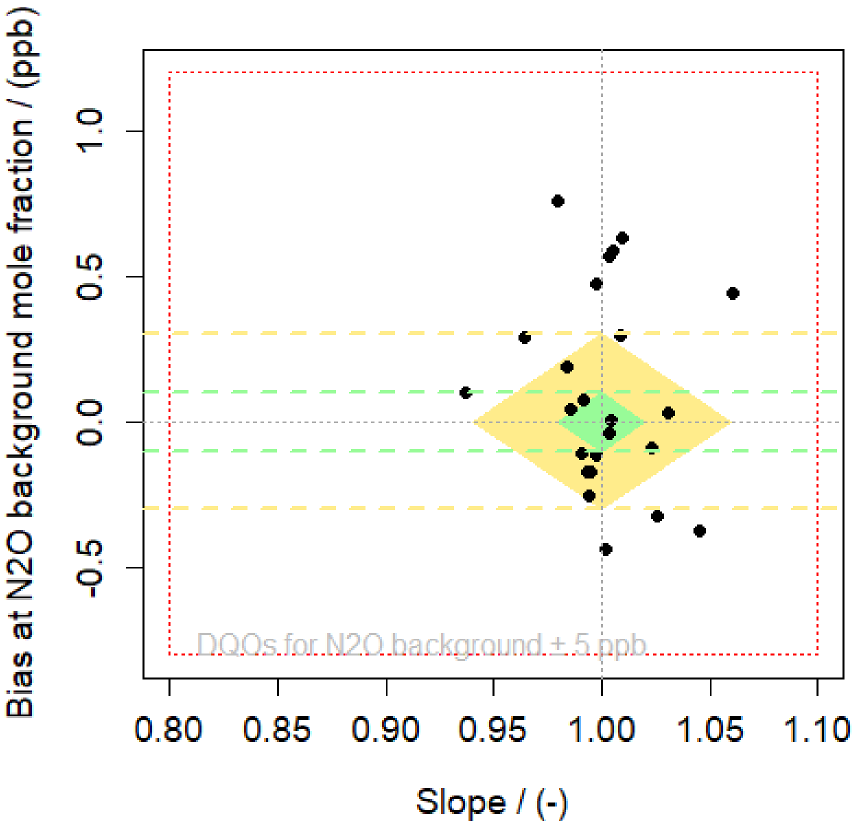
- 6th round robin (2014/15), 25 laboratories, 2 standards with average N_2O mole fraction close to ambient.
- Same analysis was made as for WCC audits.
- Results are very similar.
- Only two (8%) laboratories were within 0.1 ppb over entire range: ICOS FCL and WCC-Empa.

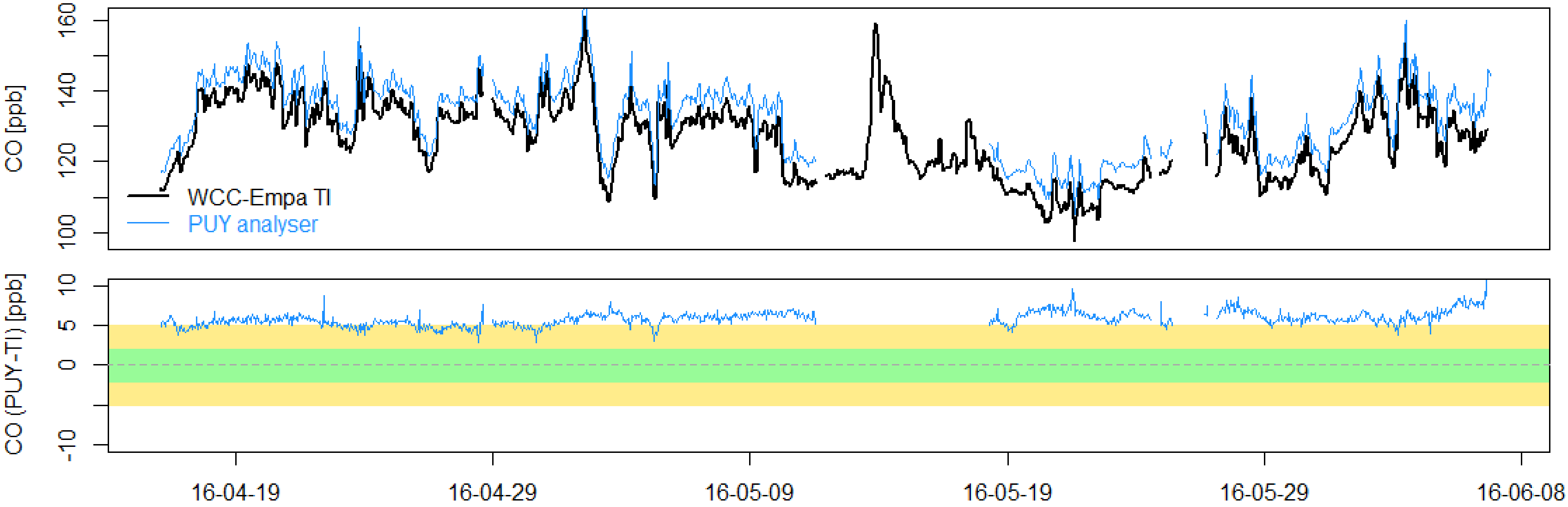






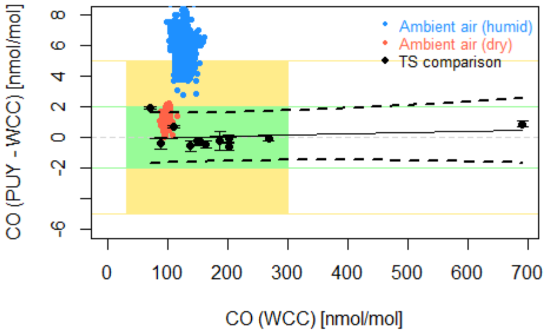
Ambient air comparison at Puy de Dôme

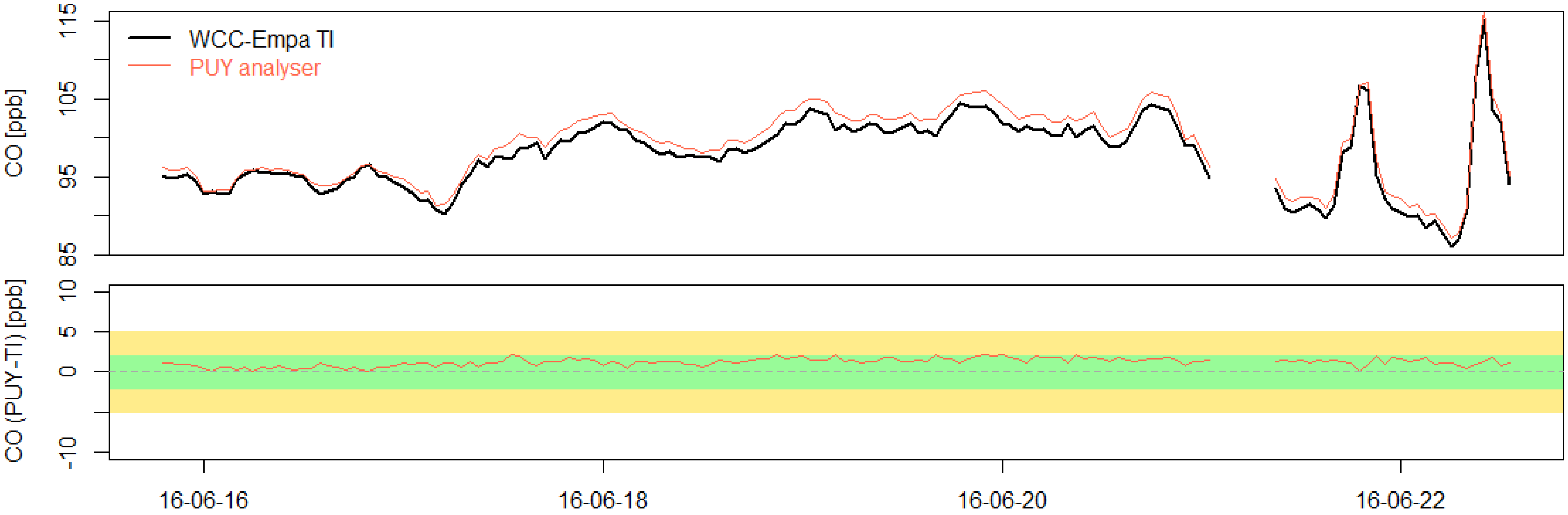
- WCC-Empa travelling instrument (TI) was measuring humid air, PUY dry air.
- Unlikely that issues with the inlet system are the cause of the bias (CO_2 and CH_4 were looking fine)
- TI has internal water vapor correction and should report dry air mole fraction.
- It seems, unlike for CO_2 and CH_4, that the internal correction is not stable over time.



Ambient air comparison at Puy de Dôme

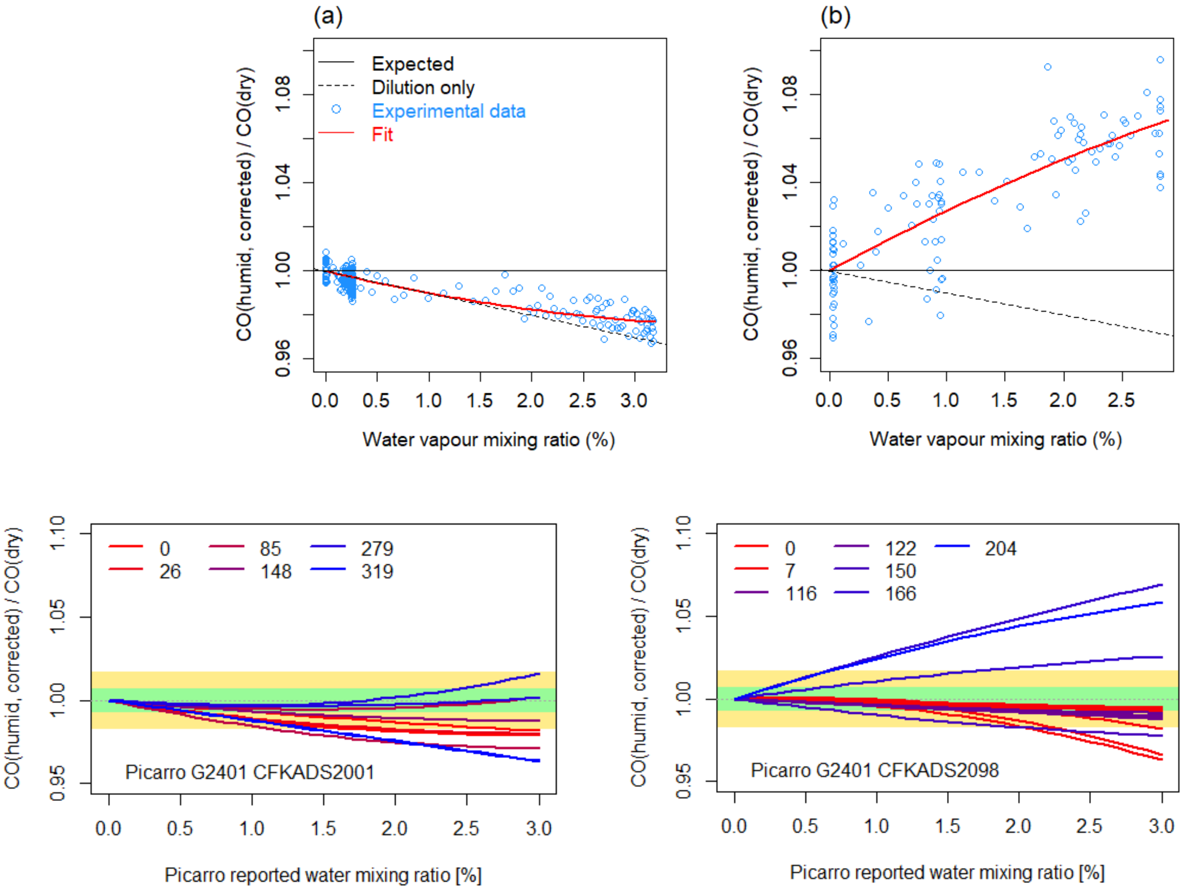
- Offset became much smaller when TI was connected to dryer.
- Bias of ambient air measurement with drying system agrees well with the comparison of standard gases.





Internal water vapor correction of the Picarro G2401

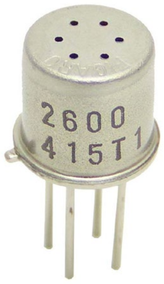
- A large change of the internal water vapor correction was observed within 4 months. (a)+(b)
- Unlike for CO_2 and CH_4, corrections are instrument specific.
- Reason for change?
- Check of the internal correction difficult, large uncertainties.
- Dry measurements recommended!
  All WCC-Empa ambient air comparisons are now made using a Nafion dryer.



Conclusions

- Spectroscopic techniques better, lower uncertainties
- As a consequence, the uncertainty of calibration standards is often a limiting factor
- Propagation of amount fraction from a calibration scales can improve compatibility within a network
- Scale approach as implemented in GAW will therefore remain important
- Standards with lower uncertainties are needed
- Comparison of WMO round robin experiment and audit results show similar results
- Independent measurements are needed to fully assess the quality of atmospheric data series

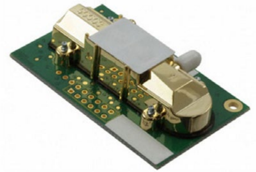
Instrument development – Low-end



Metal oxide
~ CHF 5
~ 1960

Electrochemical
/ voltammetric
~ CHF 50
~ 1980

Photochemical
~ CHF 200
~ 1990



Micro-optical
> CHF 100
~ 2000

Sensor → Micro-electro-mechanical (MEMS) type device

Integration into units, p, T, communication, multiple sensors

- Sensors: Challenging component diversity. Mainly ‘old’ technologies.
- Technical information provided by manufacturers often not sufficient.

WMO/GAW recommendations on low-cost sensors

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Low cost air pollution sensor networks are an appealing new technology for use in both research and operational applications. They offer the potential to greatly increase the spatial resolution of observations, provide localized validation of models and more precise estimates of human exposure, particularly in locations that do not have traditional monitors.

Initiated by the Scientific Advisory Group for Reactive Gases, recommendations concerning the use of LCS were made:

- **Low-cost sensors for the measurement of atmospheric composition: overview of topic and future applications**
  (WMO Report No. 1215)
  Lead authors: SC Candice Lung, Rod Jones**, Christoph Zellweger**, Ari Karppinen, Michele Penza, Tim Dye, **Christoph Hüglin**, Zhi Ning, Alastair C. Lewis, Erika von Schneidemesser, Richard E. Peltier, Roland Leigh, David Hagan, Olivier Laurent and Greg Carmichael
  Contributing authors: Gufran Beig, Ron Cohen, Eben Cross, Drew Gentner, Michel Gerboles, Sean Khan, Jesse Kroll, Pierpaolo Mudu, Xavier Querol Carceller, Giulia Ruggeri, Kate Smith and Oksana Tarasova

- **Reactive Gases Expert Group: Technical advice note on lower cost air pollution sensors**
  Alastair C Lewis, Christoph Zellweger, Martin G Schultz, Oksana A Tarasova and Reactive Gases Science Advisory Group, GAW

Both documents are available from the WMO/GAW website and give recommendations / guidance on the use of LCS.

A Follow-up discussion forum exists at https://wmoairsensor.discussion.community/

Thank you!

Acknowledgments

- Financial support of GAW activities by MeteoSwiss
- WCC-N_2O for data sharing and collaboration
- Staff at various GAW stations and Empa for their support