Summing Up 13 Years of Intercomparison Activities of the World Calibration Centre at Empa (WCC-Empa): Methane, Carbon Monoxide and Ozone

C. Zellweger, J. Klausen, and B. Buchmann
Empa, Swiss Federal Laboratories for Materials Testing and Research
Laboratory for Air Pollution / Environmental Technology, Überlandstrasse 129, CH-8600 Dübendorf

Global Atmosphere Watch WCC-Empa

EMPA Materials Science & Technology

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Federal Department of Home Affairs FDHA
Federal Office of Meteorology and Climatology MeteoSwiss

Introduction

Empa operates the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane since 1996 as a Swiss contribution to the GAW programme (funded by MeteoSwiss). To date 49 audits were made at mainly global GAW stations (Figure 1). The purpose of these audits is to ensuring traceability to a common reference [1], as illustrated in Figure 2.

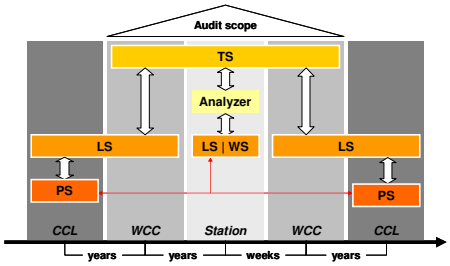

Figure 2: *Traceability chain for methane and carbon monoxide audits (ozone analog with traveling standard instrument) .*

Methane

Recommended comparability: ± 2 ppb [4]

Audit results show that the DQOs are fulfilled at most sites. The agreement between stations and WCC-Empa improved over time (Figure 3). However, individual instruments show different reproducibility (Figure 4). GC/FID systems showed a relative standard deviation ranging from 0.02% to more than 0.3%, whereas the relative standard deviation of all tested Picarro CRD instruments was lower than 0.02% based on 1-minute averages. Consequently, WCC-Empa uses this technique for traveling standard calibration to further minimize the influence of instrumental uncertainty.

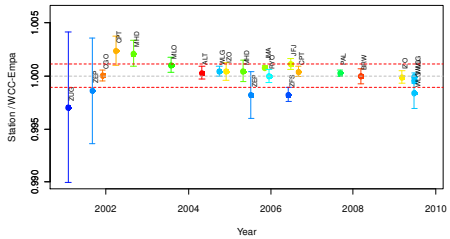

Figure 3: *WCC-Empa methane audit results. The red lines correspond approx. to the DQO limits (deviation of 2 ppb at a mixing ratio of 1800 ppb).*

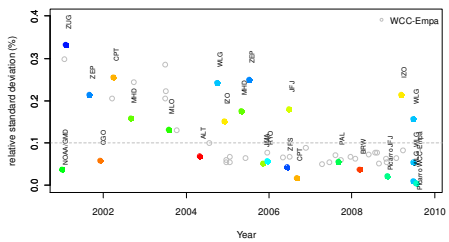

Figure 4: *Repeatability of methane instruments at GAW sites expressed as relative standard deviation of multiple injections of reference gases in %. The performance of the WCC-Empa lab GC (open circles) and data of Picarro CRDS analyzers are also shown.*

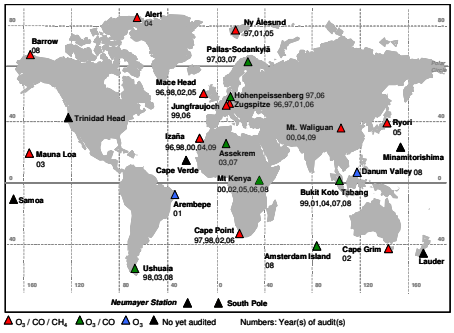

Figure 1: *Audits by WCC-Empa. Red triangles (O_3, CO, CH_4), green (O_3, CO), blue (O_3); Stations with black triangles have not yet been audited. The numbers refer to the year the audit(s).*

Carbon monoxide

Recommended comparability: ± 2 ppb [4]

Audit results often show large deviations between measurements at GAW stations and WCC-Empa (Figure 5). Part of this can be explained by scale issues, and results improve when station data are converted to the WMO-2000 CO scale (Figure 6).

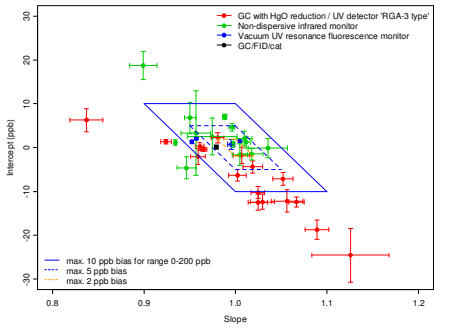

Figure 5: *Intercept vs. slope for CO audits conducted by WCC-Empa between 1997 and 2008 for different measurement techniques. The intercept / slope pairs are referenced against the WCC-Empa CO standard (calibrated traveling standard, WMO-2000 CO scale). The rhomboids displayed cover the range of slope-intercept combinations for a maximum of 2, 5, or 10 ppb bias for the concentration range 0-200 ppb CO.*

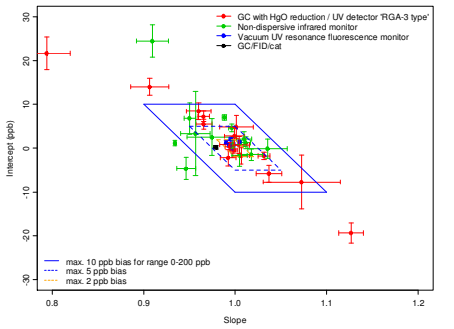

Figure 6: *Same as above, but with correction for WMO-88 and CSIRO CO calibration scales.*

References within GAW

All audits by WCC-Empa are traceable to the GAW references maintained and provided by the corresponding Central Calibration Laboratory (CCL).

Surface Ozone

CCL: National Institute for Standards and Technology (NIST)
Reference:
Standard Reference Photometer SRP#2

Carbon monoxide and methane

CCL: NOAA-ESRL
Reference:
CO: WMO-2004 carbon monoxide scale [2]
CH_4: NOAA-04 methane scale [3]

Surface ozone

DQO [1]: ≤ 20 ppb: Sufficient: 2.1 ppb + 3%
Good: 1.8 ppb + 2%
> 20 ppb: Sufficient: 1.3 ppb + 7%
Good: 1.4 ppb + 4%

Most stations fulfill DQOs, but differences between instrument types can be seen (Figure 7).

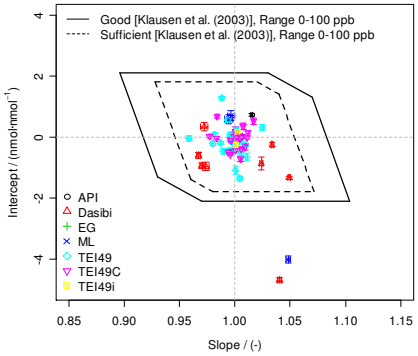

Figure 7: *Intercept vs. slope for ozone audits conducted by WCC-Empa between 1996 and 2008.*

Conclusions & Outlook

- WCC-Empa audit results since 1996 showed that mainly CO measurements are still problematic, whereas usually good results are obtained for methane and surface ozone inter-comparisons.
- The recommended comparability of ± 2 ppb is often not reached for CO. The reasons are calibration scale and analytical issues.
- DQO for surface ozone should be revised.
- The agreement between the audited stations and WCC-Empa improved over time for all parameters because of better analytical techniques and analyzers and/or the impact of WCC-Empa audits.
- New analytical techniques such as CRDS for methane greatly improved measurement capabilities both at stations and in the lab.
- WCC-Empa plans to host and operate the WCC-CO2 (audits) with a mandate to conduct system and performance audits at Global GAW stations beginning in 2010.

Contact

Christoph Zellweger
christoph.zellweger@empa.ch

References

[1] Klausen, J., et al. (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res.-Atmos., 108*, 4622, doi:4610.1029/2003JD003710.
[2] Novelli, P. C., et al. (2003), Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, *J. Geophys. Res.-Atmos., 108*, 4464, doi:4410.1029/2002JD003031.
[3] Dlugokencky, E. J., et al. (2005), Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.-Atmos., 110*, Article D18306
[4] WMO, 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, GAW Report No. 186. 2009.