LAC-IC 2018: Evaluation of the first IAEA regional water $\delta^{18}O/\delta^{2}H$ interlaboratory comparison exercise

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Motivation

- Data accuracy challenge for Global Network of Isotopes in Precipitation (GNIP):

  “The measurements in GNIP have a long-term uncertainty of about ±0.1 ‰ for $\delta^{18}O$ and ±0.8 ‰ for $\delta^{2}H$, at one standard deviation.“

- Only benchmark: proficiency tests on ~quadrennial schedule (WICO 2016, 2020)

Retrospective: WICO 2016

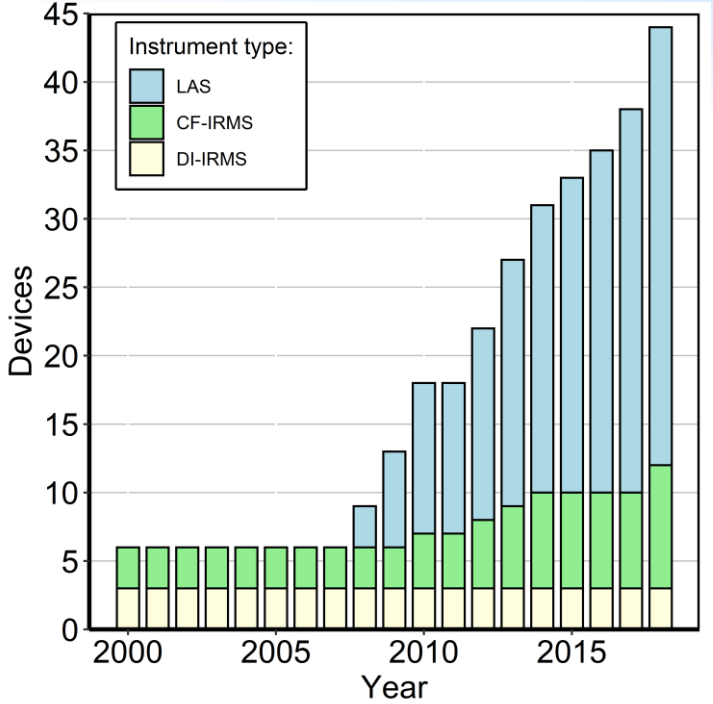
- Global PT with 235 labs, ca. 60% LAS (Wassenaar et al. 2018)
- Similar performance for LAS and CF-IRMS labs
- No conclusion on identifying good and poor performance

LAC-IC Rationale

- Easy access to $\delta^{18}O$ and $\delta^{2}H$ needed
- Rapid proliferation of devices in the region with advent of LAS
- Data reliability and comparability?

Steps:

- Pre-survey of laboratories
- Regional proficiency test
- Disentangle the „known unknowns“



Devices available in the region 2000-18
(Terzer-Wassmuth et al., accepted manuscript)

Pre-survey (early 2018)

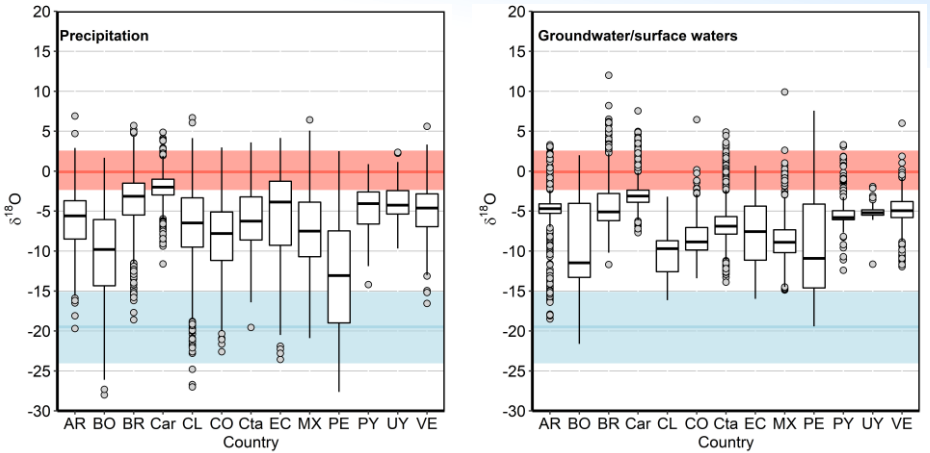
- Distributed in English and Spanish languages to 37 labs
- Instrumentation
  - Type, age, peripherals
- Human resources
  - Skill level and experience
  - Self-assessment of PI's
  - Sample throughput
- Reference materials
  - Primary RMs and access, handling
  - Secondary RMs, storage, range
  - Use of control samples
- Post-processing
  - Software used
  - Corrections applied
  - Acceptance criteria
- WICO 2016 participation

Pre-survey results (I)

- 44 instruments in 37 labs
  - 32 LAS with autosampler, mostly 8-9 injections
  - 12 IRMS, most CO_2 or H_2 equilibration
- Human resource:
  - Only 45% ranked overall experience as „intermediate to high“ or „high“
- Throughput
  - Only 20% analyse 1500/yr or more
- Working RMs:
  - see next slide
- Data processing:
  - All used multipoint calibration
  - 60% used controls regularly
  - 52% used LIMS (USGS) or LIMS for Lasers (USGS/IAEA)
  - 85% chose appropriate corrections
  - Only 27% could state their typical uncertainties

Pre-survey results (II)

- Primary RMs:
  - 80% use IAEA or USGS primary RMs
- Working RMs:
  - Most use steel barrels or glass flasks
  - 20% had bracketing ranges of < 10 ‰ $\delta^{18}O$
- Only 44% were able to bracket the span of their country.
  - Most issues with enriched bracket.



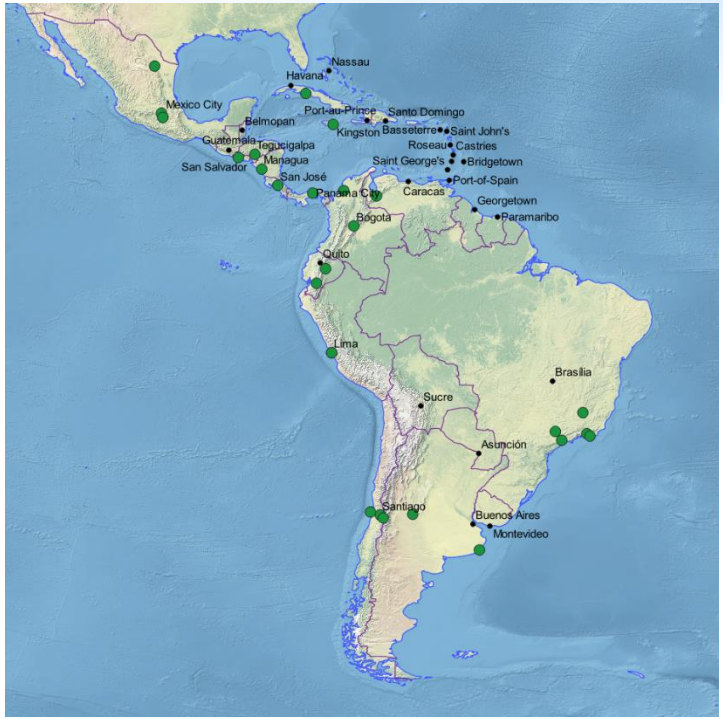
Country-based $\delta^{18}O$ ranges.
Red/blue lines/shades: Median/IQR of enriched/depleted working RMs.
(Terzer-Wassmuth et al., accepted manuscript)

Proficiency test (2018/19)

- Test schedule
  - Samples sent out November 2018
  - Reporting deadline in March 2019
  - (individual extensions granted)

- 3 samples sent to 28 labs
  - $\delta^{18}O$ between -0.96 and -15.31 ‰
  - $\delta^{2}H$ between -2.5 and -110.3 ‰

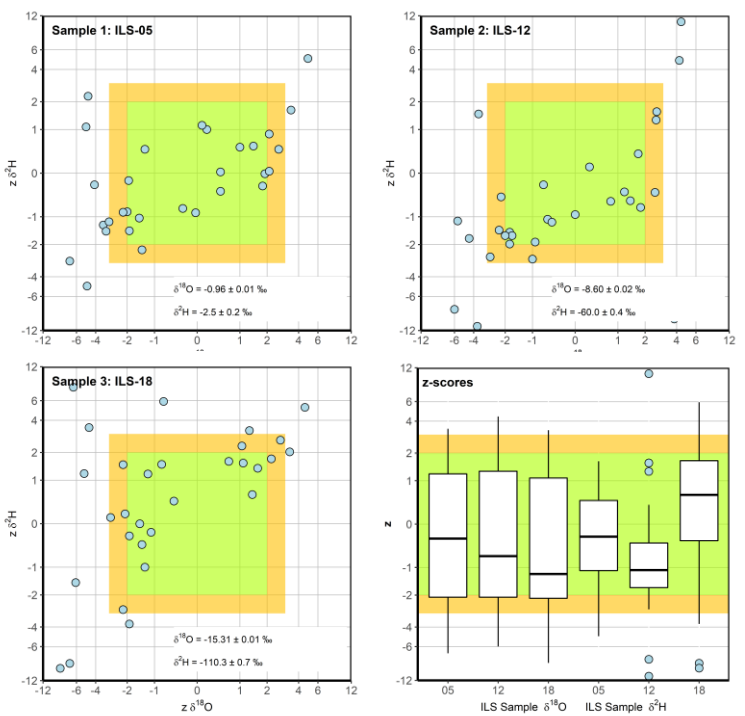
- 25 labs returned
  - 21 LAS, 3 CF-IRMS, 1 both



Map of participating laboratories (green dots)

Proficiency test results (I)

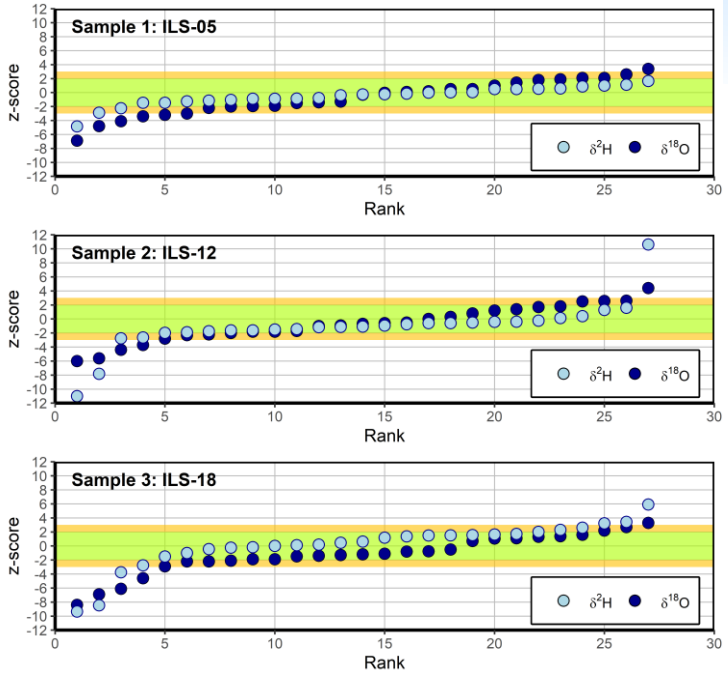
- Assessment
  - Z-score $z = \frac{x - x_a}{\sigma_p}$
  - Zeta-score $\zeta = \frac{x - x_a}{\sqrt{{u_x}^2 + {u_{x_a}}^2}}$
- SDPA
  - σ_p for $\delta^{18}O$: 0.1 ‰
  - σ_p for $\delta^{2}H$: 0.8 ‰
- Benchmarks:
  - Acceptable: |z| ≤ 2 (green)
  - Questionable: 2 < |z| < 3 (orange)
  - Unacceptable: |z| ≥ 3



Test samples and Youden dual-isotope plots (Terzer-Wassmuth et al., accepted manuscript)

Proficiency test results (II)

- Participants received individual lab reports in May 2019
- Major biases and eventual causes highlighted
- S-plots confirm Youden plots: Biases are smaller for δ^2H

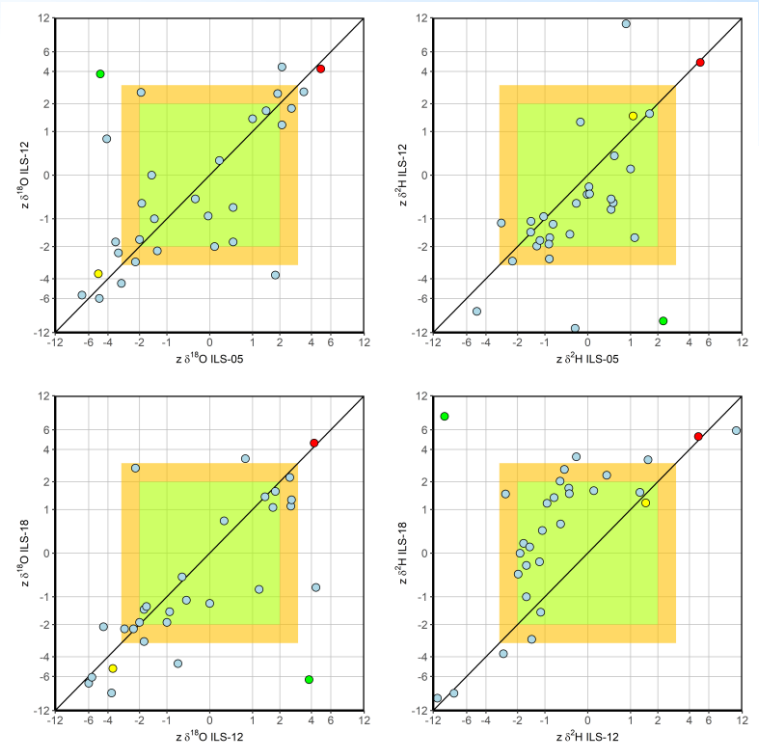


S-plots of z vs. rank
(Terzer-Wassmuth et al., accepted manuscript)

Proficiency test results (III)

Youden crossplots for „neighbouring samples“ reveal systematic biases:

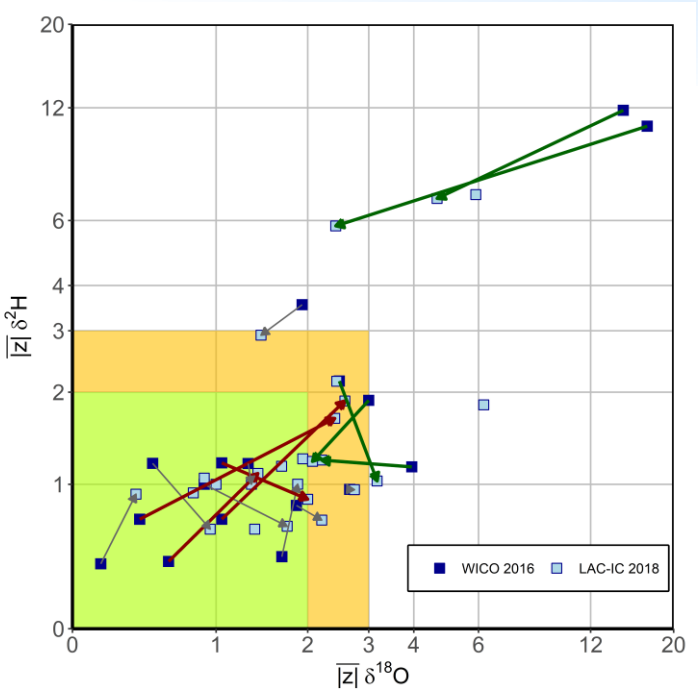
- Ficticious examples:
  - Red: Mis-calibrated reference standards for both $\delta^{18}O$ and $\delta^{2}H$ (affects both at similar magnitude and directions)
  - Yellow: Problems with one isotope (maybe instrumental, e.g. uncorrected $\delta^{18}O$-H_2O linearity on OA-ICOS)
  - Green: Unsystematic biases
- Grey: LAC-IC participants



Youden plots for „neighbouring“ samples (Terzer-Wassmuth et al., accepted manuscript)

„Proficiency trajectory“

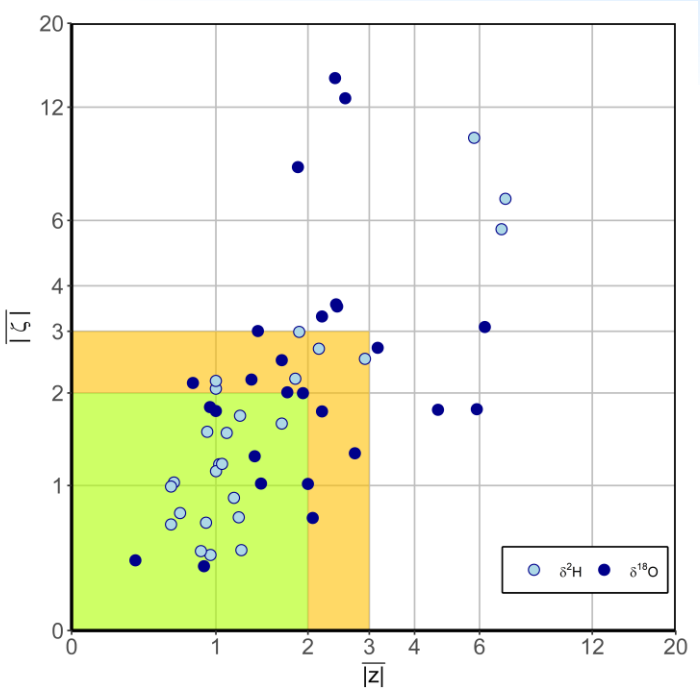
- Related LAC-IC to WICO 2016
- Mean |z| of $\delta^{18}O$ and $\delta^{2}H$ as a measure of “overall performance”.
- |z| for WICO 2016 recalculated with the σ_p of LAC-IC
  - Green arrows include improvement ($\Delta\overline{|z|} < -1$),
  - red arrows otherwise ($\Delta\overline{|z|} > 1$)
- (All participants consented to this.)



(Terzer-Wassmuth et al., accepted manuscript)

Self & outside assessment

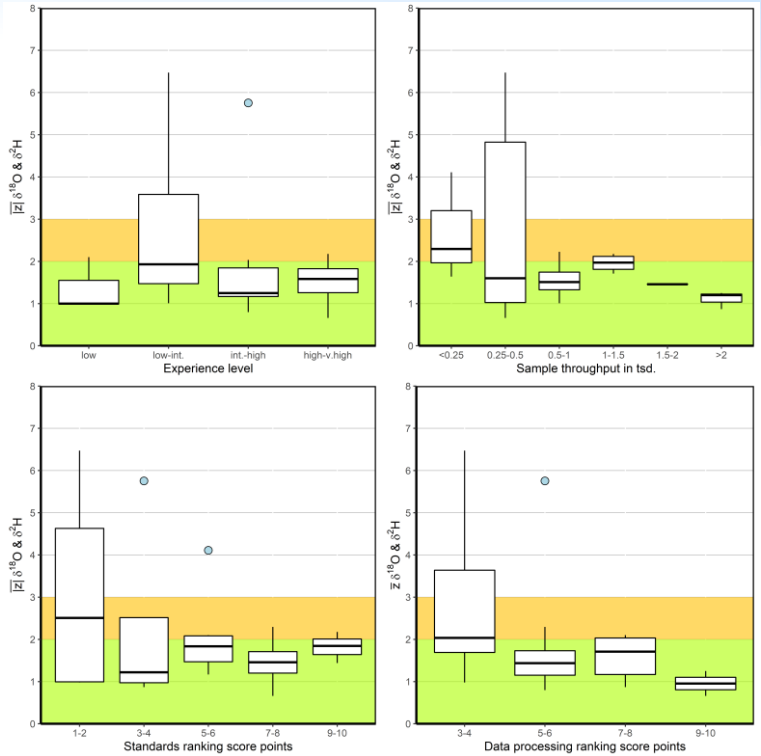
- Do submitters realistically state uncertainty?
- Cumulative z- vs. ζ-scores
- Upper left: Satisfactory or questionable results but over-optimistic uncertainty reporting
- Lower right: Realistic assessment of large biases



(Terzer-Wassmuth et al., accepted manuscript)

Causes of performance

- Experience level would deem logical but couldn‘t be sustained
- Sample throughput
- RM availability and handling (expert score ranking)
- Post-processing techniques (expert score ranking)



(Terzer-Wassmuth et al., accepted manuscript)

Conclusions

- Contributing factors for good and poor performance identified
- Assess throughput before buying
- Have an eye on laboratory RMs (primary and working)
- Robust data treatment and training therein (no black box!)

WICO 2020 in the making…

Acknowledgements & References

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- References:

  - Terzer-Wassmuth et al. (accepted manuscript): The first IAEA inter-laboratory comparison exercise in Latin America and the Caribbean for stable isotope analyses of water samples. Isotopes in Environmental and Health Studies.
  - Wassenaar et al. (2018): Seeking excellence: An evaluation of 235 international laboratories conducting water isotope analyses by isotope-ratio laser-absorption spectrometry. Rapid Communications in Mass Spectrometry (32), 393-406

IAEA
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Thank you!