How good are my stable isotope data? Implications on using an in-house QC system for stable isotope measurements

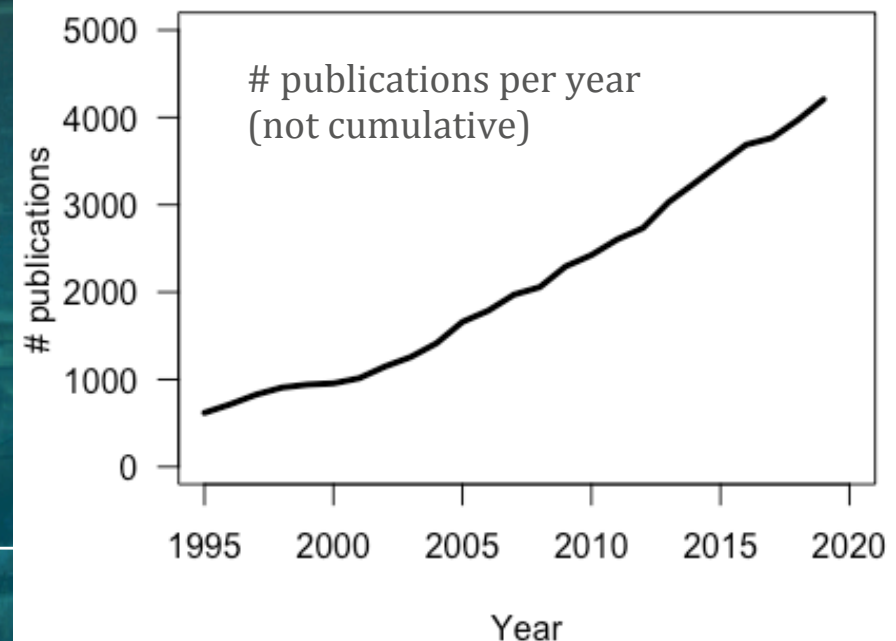**David X. Soto**[1], Sergey Assonov[2], Helen Grant[1], M. Glória Pereira[1], and Ales Fajgelj[2]

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EGU – May 2020
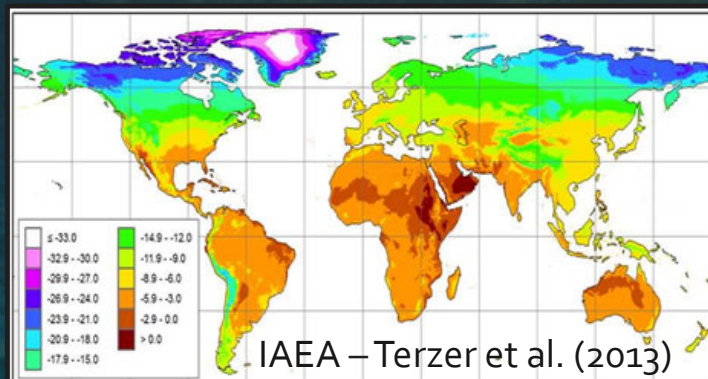
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Stable isotope measurements

- Stable isotopes are widely used with applications in forensics, ecology, biogeochemistry, atmospheric sciences, and hydrology.

- Isotope data in the recent years has increased considerably and a demand of high-quality isotope data is required.

- It is difficult to compare different isotope datasets, which might have been produced using different protocols, and even different calibration and normalization approaches.
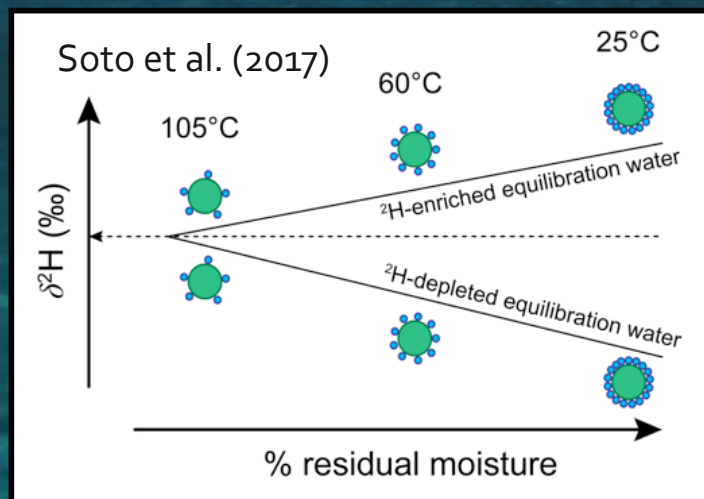

ice core data

Photo credit: H.Roop, NSF

publications per year (not cumulative)

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Data comparability

- For example, global water isoscapes, ice cores, materials with exchangeable H, and many more…

IAEA – Terzer et al. (2013)

Isoscapes (e.g. GNIP)

- Standardized methods for representative sample

- Data quality tools – [see D497 - EGU2020-22653]

Soto et al. (2017)

Organic materials with exchangeable H

- Differential protocols and calibration approaches [see D493 - EGU2020-9674]

- NMR vs. IRMS – [see D494 - EGU2020-11630]
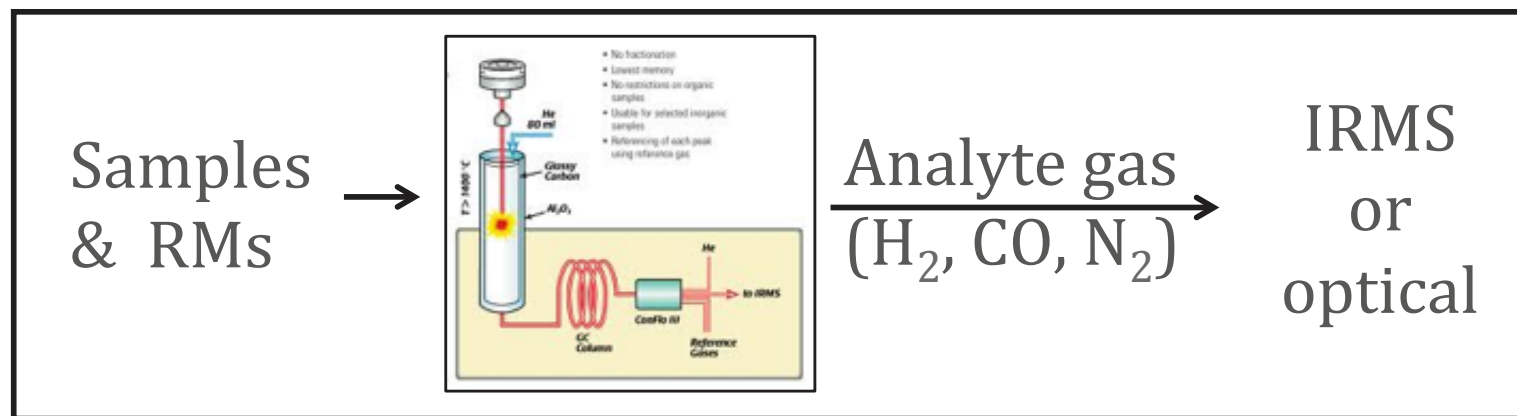
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Quality Management System

Internal Quality Control tools are needed in research and service laboratories to support isotope data quality (e.g. ISO 17025)

- Metrological traceability [see D499 - EGU2020-22382]

- Uncertainty estimation (incl. operator errors)

- Quality control tools

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Uncertainty estimation

- Uncertainty calculations may be complicated by various and not well-controlled factors, including sample matrix effects, incomplete reactions and by-products formed etc. (<u>external precision</u>).

- The use of data scatter (e.g. SD of Reference Materials (RMs) and in-house working standards) as a measure of uncertainty is obviously insufficient.

- When establishing target uncertainty values, standard specifications should be considered.
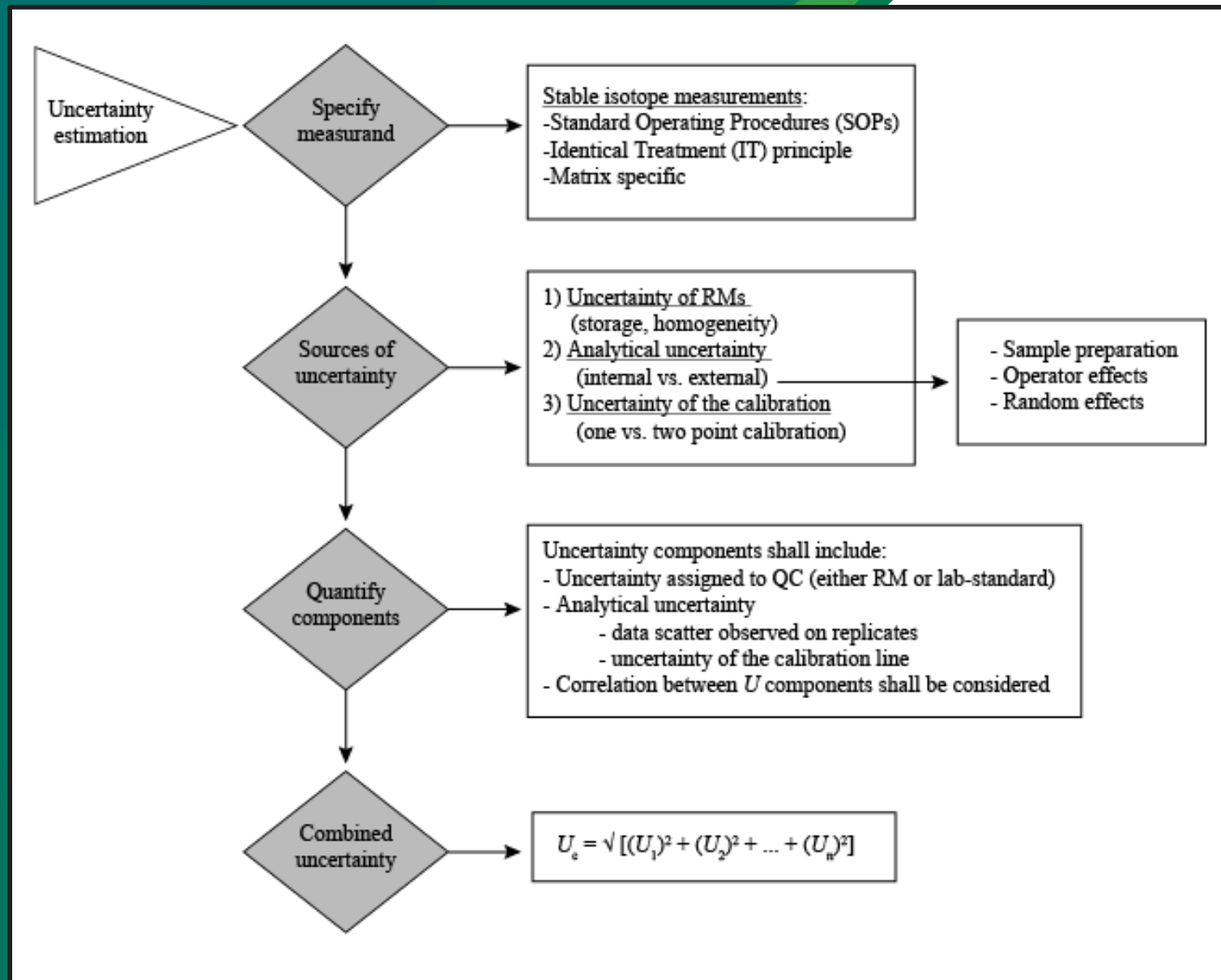

Samples & RMs → [instrument diagram] → Analyte gas (H_2, CO, N_2) → IRMS or optical

"External"   vs.   "Internal"

Uncertainty estimation

Uncertainty vs. "fit-for-purpose"

- Any isotope laboratory shall establish "target" uncertainty as based on intended data use.

- However, correctly estimated uncertainties can reduce the probability of obtaining significant differences between groups of unknowns, which the purpose of the analysis could not fit. → e.g. low uncertainty for carbonate RMs [see D506 - EGU2020-11525]

Reduce uncertainty: e.g.
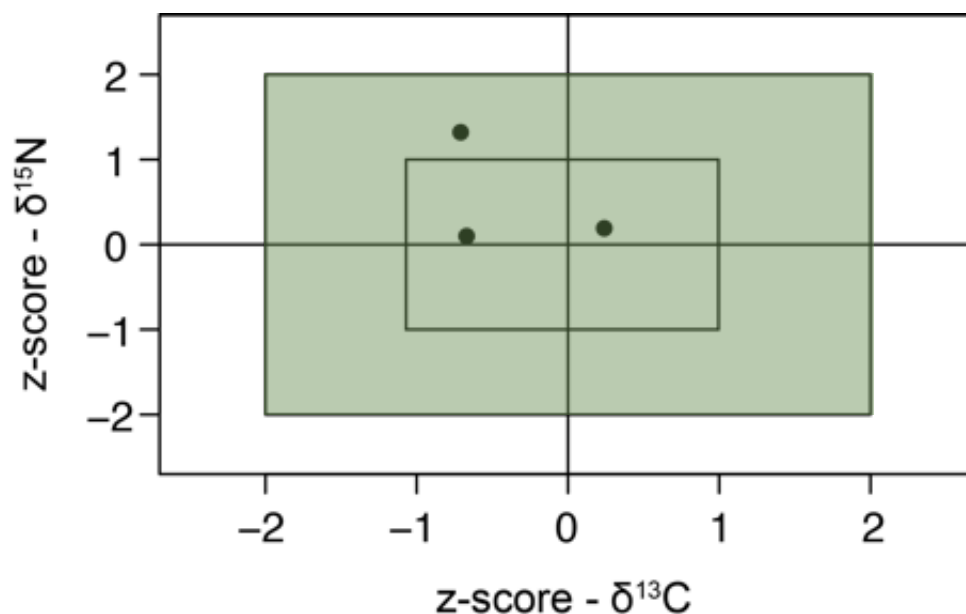- Improved instrumentation
- Enhanced calibration

Specific protocol: e.g.
- matrix specific
- needed uncertainty for application

Quality Control tools

- Performance based on QC materials can be estimated by using the z-score criteria developed for proficiency tests (z-score <2):
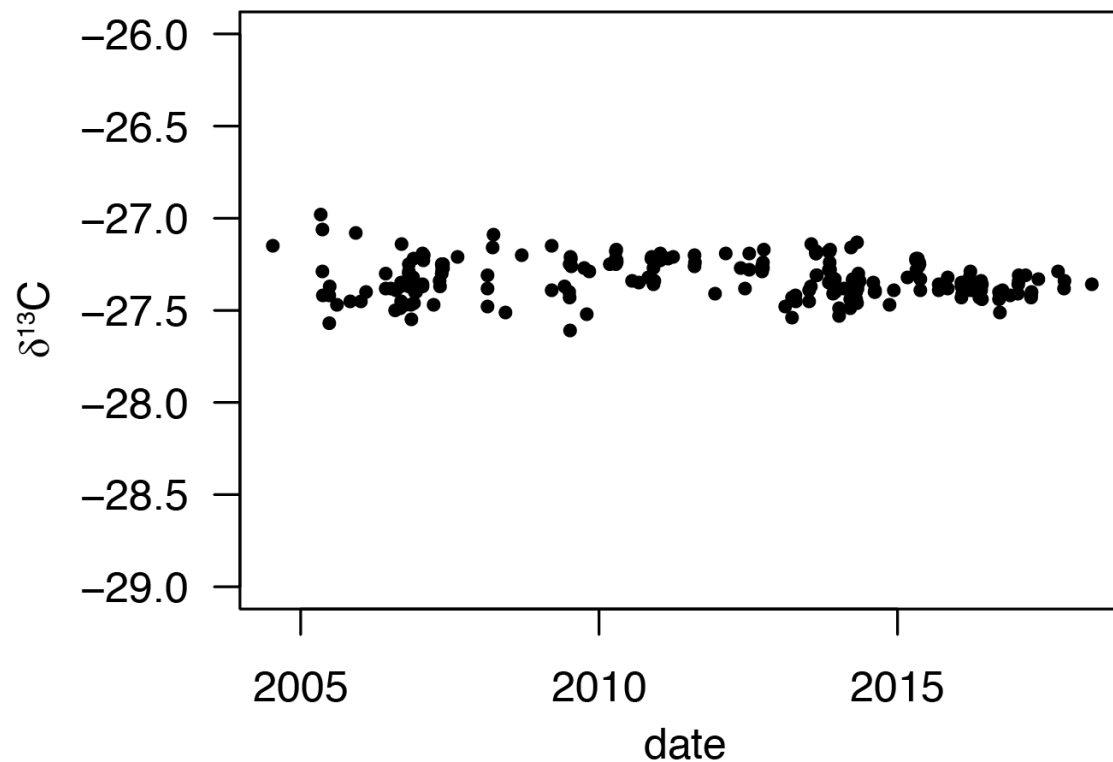
$$z\text{-}score = [\delta^i X_{QM\text{-}assigned} - \delta^i X_{QM\text{-}observed}] / U_{QC\text{-}combined}$$

Data from Assonov et al (2019) - EGU2019-16776

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Quality Control tools

- Control charts:
    - the criteria to revise <u>limits of QC standards</u> in an objective manner including the removal of outliers.
    - <u>Warning and action limits</u> depend on isotopic composition, homogeneity, and statistical approach → <u>uncertainty estimation</u>

Criteria to revise limits of QC standards

- Outlier removal?
- Which period of data?
- long-term data vs. one calibration data with U propagation?

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Conclusions

- Establishing target-uncertainty, as related to intended data use (applications) is required.

- As QC, one shall take a similar-to-samples material, available in large amounts. One may suggest to run it regularly, in particular after changing (major) operational parameters gas flow, O_2 flow, etc.

- When results on QC materials are outside warning limits and action limits, this shall trigger the need of further investigation and remedial actions.

- For example, material heterogeneity or difficulty of combustion for complex materials can cause data to be outside limits. Realistic uncertainty estimation of the method to be used in accordance of the established target uncertainty must be determined.

- When stable isotope measurements are used, implementation of these protocols are of great relevance for a well-balanced decision making based on the use of isotope results.

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The Stable Isotope Laboratory at UKCEH – Lancaster site

Thank you

Any questions?

Please email to : dsoto@ceh.ac.uk

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