Reproducible
Research
Workshop

Data handling in molecular geography

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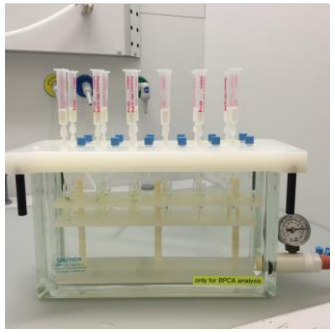
Uncertainty of measurements

"All measurements, however careful and scientific, are subject to some uncertainties. Error analysis is the study and evaluation of these uncertainties."

J.R. Taylor, 1982. *Error analysis.*

Origins of errors

Inverse relationship	Decreasing sample amount → Increasing potential errors			
Typical sample mass (g)	10^{1} to 10^{3}	10^{-3} to 10^{-2}	10^{-4} to 10^{-3}	10^{-5} to 10^{-4}
Work step	Sampling 	Preparation 	Extraction 	Measurement 
Sources of errors	Sampling devices	Lab tools	Chemical reagents	Instrumentation

Two classes of errors

Instrumentation

- Depending on the sensitivity of the analytical device
- Quantification of uncertainty via calibration procedures

Sampling and analytical uncertainty

- Depending on the sample size and number of sample transfer
- Quantification of uncertainty via external standards

Organic geochemistry using isotopes

Molecular investigations in complex matrices (often << 1 g kg^{-1})

1. Extraction of compound classes
2. Identification of molecular structures using chromatography
3. Isolation and concentration of target compounds
4. Measurement of the isotopic composition using mass spectrometry
5. Data handling

Model of constant contamination

Statistical approximation of theoretical and observed frequencies

Key features

- Every measurement campaign is affected by the same error
- Extraction of error allows for the correction of data

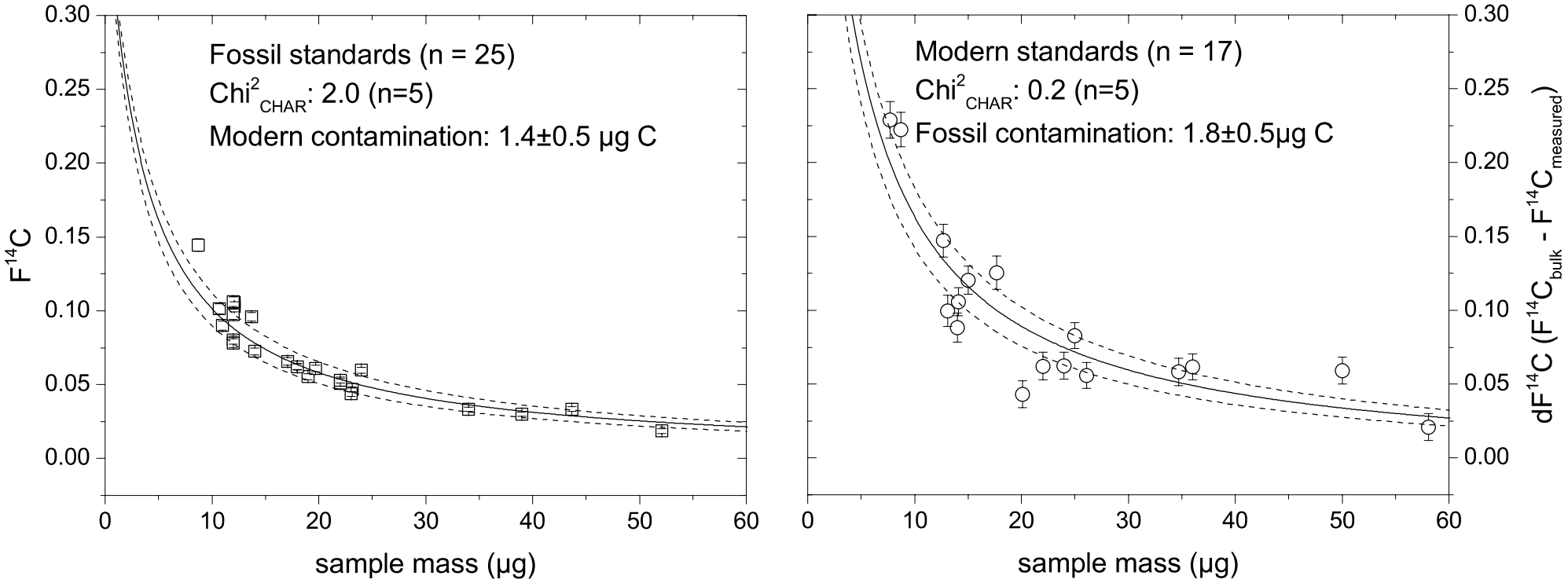
$$F^{14}C_s = \frac{F^{14}C_m * m_m - F^{14}C_c * m_c}{m_m - m_c}$$

Error propagation yields:

$$\sigma^2_{F^{14}C} = \left[\sigma_{m_c}\left(\frac{F^{14}C_m * m_m - F^{14}C_c * m_c}{(m_m - m_c)^2}\right) - \left(\frac{F^{14}C_c}{(m_m - m_c)}\right)\right]^2 +$$

$$\left[\sigma_{m_m}\left(\frac{F^{14}C_m}{(m_m - m_c)} - \frac{F^{14}C_m * m_m - F^{14}C_c * m_c}{(m_m - m_c)^2}\right)\right]^2 + \left[\sigma_{F^{14}C_m}\frac{m_m}{m_m - m_c}\right]^2 + \left[\sigma_{F^{14}C_m}\frac{-m_c}{m_m - m_c}\right]^2$$

Sensitivity test by means of (AMS) accelerating mass spectrometry



Summing up

- All physical measurements are subject to errors (even if they are negligible)
- Uncertainties increase with decreasing sample size (Gt → ng)
- Errors originate from sampling, laboratory handling and instrumentation
- Standard materials, reference samples and calibration procedures enable high precision
- ‘Error analysis‘ allows for extraction of errors and subsequently correction of data