Uncertainty from Sampling - *Evaluation and use in Validation*

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Overview

- Objectives
  + Role of new Eurachem/Eurolab/Citac/Nordtest Guide

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Traditional Approach to Sampling Quality

- Sampling traditionally considered separately from measurement.
- Design ‘correct’ sampling protocol to give a representative sample
- Train sampler to apply the protocol,
- Assume that is applied ‘correctly’
  - no quality control of sampling
- Assume that uncertainty of measurement arises only in the lab analysis

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Sampling as part of the measurement process

- Sampling really the first step in the measurement process
- *In situ* measurement techniques reveal this
  - Place the sensor→ make measurement = taking a sample
  - Uncertainty in sampling produces U in measurement
- Physical sample preparation (in field or lab)
  - e.g. filter, acidify, dry, store, sieve, grind, split
  - is also part of the measurement process
  - and potentially important source of U
  - include in the validation process

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Sampling as part of the measurement process

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Sampling as part of the measurement process

- If the objective is to measure the true value
  - of the analyte concentration (or measurand)
  - in the sampling target *(e.g. batch of food)*
- Sampling is included in measurement process
- U from sampling part of measurement uncertainty*
  - method validation needs to include sampling
- If true value (or measurand) defined solely in terms of laboratory sample
  - sampling is not included
- Most user of analytical measurements assume x ± U apply to target, not just to lab sample
  - * Ramsey MH (2004) Accred Qual Assur., 9, 11-12, 727 - 728

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Methods for estimating uncertainty of measurement *(including sampling)*

- What are the options?
  - Empirical methods - 'Top down' approach
    - based on replicate measurements (within or between organisations)
    - *applicable to any system*
  - Modelling methods - 'Bottom up' approach
    - based on identifying, estimating and summing all of the components = 'Budget Approach'
      - (Kurfurst *et al*, 2004, Accred Qual Assur., 9, 64-75)
    - sometimes uses Sampling Theory (e.g. Gy's) to estimate components
      - (Minkkinen 2004, Chemometrics and Intelligent Lab. Systems, 74, 85-94)
      - *applicable to some particulate systems*

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Estimation of uncertainty – contributions in the empirical approach

Process	Effect class	
	Random *(precision)*	***Systematic*** *(bias)*
Analysis	*e.g. duplicate analyses*	*e.g. certified reference materials*
Sampling	*duplicate samples*	*Reference Sampling Target, Inter-Organisational Sampling Trial*

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Statistical model
for empirical estimation of uncertainty

x = *measured* value of the analyte concentration in the sampling target

= *true* value of the analyte concentration in the sampling target

‘W’ Sampling Design for Lettuce

Nitrate conc. in Duplicate Samples

Most analytical duplicates

Validation of whole measurement procedure

Initial validation

-used when sampling is done as a one-off campaign

-(spot sampling, e.g. contaminated site investigation)

-use initial estimation of U

-e.g. using duplicate method - requiring ≥32 measurements

-One target/site validation may need repeating at intervals

-i.e. repeated sampling, (e.g. time or flow- proportional sampling of waste water).

Validation demonstrates what can be achieved and,

-if that conforms to fitness-for-purpose requirement,

-then procedures deemed suitable for routine use.

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Relationship between validation and quality contro

of whole measurement procedure

Quality control of sampling (and analysis) SAQC

- to ensure that conditions prevailing at validation
- and therefore the expected uncertainty attached to the results)
- are still applicable every time those sampling/analytical procedures executed.
- i.e. routine measurements are still fit-for-purpose

Differences between sampling and analytical validation/QC

- Some sampling targets (like analysis?) quite consistent between batches (e.g. water in butter)
- Many targets are very variable between 'batches' (e.g. contaminated land – hetero)
- Estimates of U, and FFP criteria (if site specific), may have varied since time of validation
- May need more elaborate SAQC – or repeated validation, at each target/batch/site

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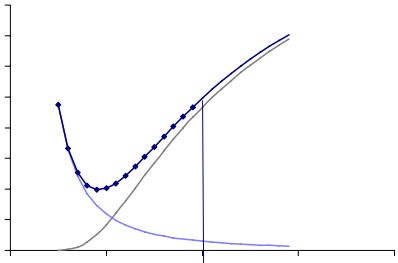
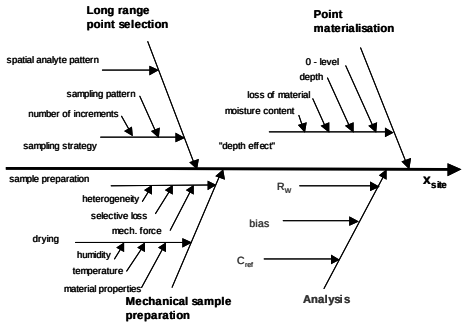
Judging fitness-for-purpose in validation

- How can you judge if you have too much uncertainty?
- One option -use the optimised uncertainty (OU) method*
- Balance the cost of measurement
  - against the cost of making incorrect decisions
- Knowing sampling and analytical components
- judge whether either is not FFP
- therefore where improvements/ increased expenditure required

Acceptable level of Uncertainty?



Cause & effect diagram
for Budget Modelling (soil sampling)



R_w is within-laboratory reproducibility

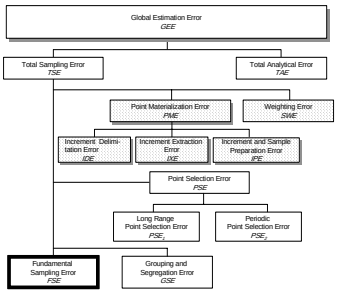
U Estimates from Budget Modelling

Effect	Relative Standard Uncertainty(%)	
	Cd	P
Variation "between locations"	5.4	2.9
Sampling strategy	1.0	0.5
Depth	3.5	3.7
Splitting	3.7	3.3
Drying	0.6	0.6
Analysis	5.2	9.7
Combined Uncertainty	**9.1**	**11.3**

Modelling using Sampling Theory

$$\sigma_r^2 = Cd^3\left(\frac{1}{M_S} - \frac{1}{M_L}\right)$$

Sampling Theory of Gy



$$GEE = TSE + TAE$$

$$TSE = (PSE + \mathbf{FSE} + \mathbf{GSE}) + (\mathbf{IDE} + \mathbf{IXE} + \mathbf{IPE}) + \mathbf{SWE}$$

U estimates from Sampling Theory

s_{r1} = 0.033 = 3.3 % …. Primary sample

s_{r2} = 0.13 = 13 % …. Secondary sample

s_{r3}

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