Overview of Uncertainty from Sampling and the UfS Guide

Michael H Ramsey
School of Life Sciences,
University of Sussex, Brighton, UK
m.h.ramsey@sussex.ac.uk

Sampling Uncertainty
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Overview

- Uncertainty (U) in measurement and sampling -
  - key parameter of measurement (and sampling) quality
- Sampling as part of the measurement process
- Methods for estimating uncertainty of measurements ‘U’ (inc. sampling)
  - Overview of Guidance from Eurachem/Eurolab/Citac/Nordtest/AMC
  - and from Nordtest Guide
- Benefits of knowing uncertainty – including:
  - New approach to quantifying sampling quality
  - Judge FFP – i.e. how much uncertainty is acceptable
  - more reliable management decisions
- Conclusions - for range of applications
Uncertainty in measurement and sampling

• U of measurement is:-
  – Informally:- the interval around the result of the measurement that contains the true value with high probability
  – Formally:-
    • An estimate attached to a test result which characterises the range of values within which the true value is asserted to lie (ISO 3534-1: 3.25, 1993)
    • Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand (ISO GUM, 1993: B.2.18)
  – Includes random and systematic effects. U ≠ precision
  – Ideally U value attached to each measurement x ± U
    • Gives user info on quality (not left in the lab!)

• U arises from all steps in measurement (e.g. sampling)
• Key parameter of measurement (and sampling) quality
• Doesn’t assume measurements (or sampling) are correct

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
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 and QC processes

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**Sampling as part of the measurement process**

<table>
<thead>
<tr>
<th>Process step</th>
<th>Form of material</th>
<th>Description of process step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling</td>
<td>Sampling Target</td>
<td>Collection of a single sample, or several increments combined into composite sample</td>
</tr>
<tr>
<td>Preparation</td>
<td>Primary sample</td>
<td>Concentration and/or splitting</td>
</tr>
<tr>
<td></td>
<td>Sub-sample</td>
<td>Further concentration and/or splitting</td>
</tr>
<tr>
<td></td>
<td>Laboratory sample</td>
<td>Physical preparation, e.g. drying, sieving, milling, splitting, homogenisation</td>
</tr>
<tr>
<td></td>
<td>Test sample</td>
<td>Selection of test portion for chemical treatment preceding chemical analysis</td>
</tr>
<tr>
<td></td>
<td>Test portion</td>
<td>Chemical treatment leading to analytical determination</td>
</tr>
<tr>
<td></td>
<td>Test solution</td>
<td>Analytical determination of analyte concentration</td>
</tr>
</tbody>
</table>

More careful use of the word ‘sample’
### 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, area of soil etc.)*
- Sampling is included in measurement process
- U from sampling part of measurement uncertainty*
  - method validation and QC 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 \( x \pm U \)
  apply to target, not just to lab sample


### 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
    - Examples in the Guide and this workshop – for food (A1, A4), soil (A2) and water (A3)
  - **Modelling methods** - ‘Bottom up’ approach
    - based on identifying, estimating and summing all of the components = ‘Budget Modelling Approach’ – Example in Guide for top soil (A6)
    - (Kurzreck et al, 2004, Accred Qual Assur., 9, 64-75)
  - sometimes Modelling using Sampling Theory (e.g. Gy’s) to estimate components in particulate systems
    - (Minkkinen 2004, Chemometrics and Intelligent Lab. Systems, 74, 85-94)
    - Example in Guide for animal feed (A5)

- **Consider application for validation and quality control stages**
Examples of estimating uncertainty of measurement (including sampling)

<table>
<thead>
<tr>
<th>Application</th>
<th>Method</th>
<th>Guide example</th>
<th>Speaker</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food</td>
<td>Empirical</td>
<td>A1</td>
<td>Mike Thompson</td>
<td>14:00 Session A</td>
</tr>
<tr>
<td>Food</td>
<td>Empirical</td>
<td>A4</td>
<td>Bertil Magnusson</td>
<td>12:30</td>
</tr>
<tr>
<td>Water</td>
<td>Empirical</td>
<td>A3</td>
<td>Christian Gron</td>
<td>15:30</td>
</tr>
<tr>
<td>Soil</td>
<td>Empirical</td>
<td>A2</td>
<td>Katy Boon</td>
<td>14:00 Session B</td>
</tr>
<tr>
<td>Soil</td>
<td>Modelling</td>
<td>A6</td>
<td>Ulrich Kurfürst</td>
<td>14:30 Session A</td>
</tr>
<tr>
<td>Animal Feed</td>
<td>Modelling</td>
<td>A5</td>
<td>Pentti Minkkinen</td>
<td>14:30 Session A</td>
</tr>
</tbody>
</table>

2 further examples in Nordtest Guide i.e.
Fe in iron ore - empirical
Conductivity in wastewater - empirical (variography)

Statistical model
for Empirical estimation of uncertainty

\[ x = X_{\text{true}} + \varepsilon_{\text{sampling}} + \varepsilon_{\text{analytical}} \]

\( x = \text{measured} \) value of the analyte concentration in the sampling target
\( X_{\text{true}} = \text{true} \) value of the analyte concentration in the sampling target
\( \varepsilon_{\text{sampling}} + \varepsilon_{\text{analytical}} = \text{effects on measured concentration from sampling and analysis} \)

\[ \text{variance of measurement} = S^2_{\text{meas}} = S^2_{\text{sampling}} + S^2_{\text{analytical}} \]
- includes between-organisational effects (e.g. sampling & analytical bias)

\[ \text{standard uncertainty} = u = S_{\text{meas}} \]
### Four empirical methods for estimating uncertainty including that from sampling

<table>
<thead>
<tr>
<th>Method #</th>
<th>Method description</th>
<th>Samplers (People)</th>
<th>Protocols</th>
<th>Component estimated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Duplicates</td>
<td>single single</td>
<td>Yes No</td>
<td>Yes No</td>
</tr>
<tr>
<td>2</td>
<td>Multiple protocols</td>
<td>single multiple</td>
<td>Yes No</td>
<td>Yes No</td>
</tr>
<tr>
<td>3</td>
<td>CTS</td>
<td>multiple single</td>
<td>Yes No</td>
<td>Yes Yes</td>
</tr>
<tr>
<td>4</td>
<td>SPT</td>
<td>multiple multiple</td>
<td>Yes No</td>
<td>Yes Yes</td>
</tr>
</tbody>
</table>

CTS = Collaborative Trial in Sampling, and SPT = Sampling Proficiency Test.

Simplest Empirical method is ‘Duplicate Method’ (#1) – applied in A1, A2, A3, A4

1 estimate analytical bias using CRM. 2 Analytical bias partially or completely included when multiple labs involved

### Budget Modelling Approach
to estimating U - Cause & effect diagram

$R_v$ is within-laboratory reproducibility
**Budget Modelling Approach**

*to estimating U*

Summation of all individual components of uncertainty
-e.g. applied to concentration of Cd and P in field of arable top soils

\[ \overline{X}_{site} = \overline{X}_{anal} \times f_{b-loc} \times f_{strat} \times f_{depth} \times f_{prep} \times f_{dry} \]

- \(\overline{X}_{site}\) = measurement result
- \(\overline{X}_{anal}\) = mean from the analysis of test samples
- \(f_{b-loc}\) = correction factor for deviation "between locations"
- \(f_{strat}\) = correction factor for bias due to sampling strategy
- \(f_{depth}\) = correction factor for the "depth effect"
- \(f_{prep}\) = correction factor for errors during mechanical sample preparation
- \(f_{dry}\) = correction factor for deviation of moisture content

\[ u_{site} = \sqrt{u_{anly}^2 + u_{b-loc}^2 + u_{strat}^2 + u_{depth}^2 + u_{prep}^2 + u_{dry}^2} \]

*Explained by Ulrich Kurfürst in Example A6*

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**Modelling using Sampling Theory**

Sampling theory of Gy defines 8 sampling errors
- includes ‘fundamental sampling error’ described by:-

\[ \sigma_f^2 = Cd^3 \left( \frac{1}{M_s} - \frac{1}{M_L} \right) \]

\[ \sigma_f = \frac{\sigma_a}{a_L} \]

- \(\sigma_f\) = Relative standard deviation of the fundamental sampling error
- \(\sigma_a\) = absolute standard deviation (in concentration units)
- \(a_L\) = average concentration of the lot
- \(d\) = characteristic particle size = 95 % upper limit of the size distribution
- \(M_s\) = Sample size
- \(M_L\) = Lot size

*Explained by Pentti Minkkinen in Example A5*
Benefits of Knowing Uncertainty

• #1: Improving reliability of decisions
  – e.g. for potentially contaminated lettuce
  – Risk assessment:
    • Hazard > threshold?,
    • Exposure > TDI?
  – Saves money on consequences of:
    • unnecessary destruction of batch = false positive
    • undetected contamination (e.g. litigation) = false negative
  – Compare different investigations - in space or time

Know the U → make more reliable decisions

- Overestimate of U - can cause unreliable decisions
- Underestimate of U

Contaminant concentration

Threshold (e.g. 4500 mg/kg)

True value

‘false positive’

‘false negative’
Effect of $U$ on interpretation

Nitrate concentrations (mg kg$^{-1}$) for routine sample (S1A1) with the associated measurement uncertainty (estimated to be $U = 16.4\%$).

e.g. Target F value of the measurand (or true value) between 4332 mg kg$^{-1}$ and 6032 mg kg$^{-1}$, = ‘Probably Contaminated’, compared with threshold 4500 mg kg$^{-1}$

Probabilistic classification has only one batch definitely uncontaminated (G), whereas deterministic classification has 4 batches uncontaminated (A, B, G & H)

Only one batch (C) is Definitely Contaminated – position taken by some regulators!

General issues discussed later by Roger Wood
Benefit #2 **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

  based upon Thompson, M. and Fearn, T (1996), Analyst, 121, 275

![Graph showing acceptable level of uncertainty](image-url)
**Benefit #3 of Knowing Uncertainty**

**Rational basis for allocation of finance,**

to:-

1. Measurement as a whole, and
2. Apportionment between sampling and analysis

Allows achievement of optimal uncertainty
- and fitness for purpose of whole measurement method
  – *e.g. lettuce in Example A1*

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**Achieving FFP at Optimal Uncertainty**

- Graph shows that U is too high – need to reduce it
- Need to know source of U
  – from sampling or from chemical analysis?
  – Duplicate Method + ANOVA - tells us sampling 78% of U
- We need to reduce the U by a factor of 2 (360 → 180)
- Sampling theory predicts (e.g. Gy’s) need to increase sample mass by factor of 4 ( = 2²)
- Reduction in U was achieved in practise → FFP
  – By taking composite sample with 40 heads instead of 10
  – Make whole method valid (i.e. suitable for routine use)
  – Full details in Lyn *et al.*, (2007) ACQUAL, 12, 67-74
Benefits #4 of Knowing Uncertainty

Provides tool for monitoring Quality of Sampling
- Better than assuming ‘correct’ sampling achieved
- Gives quantitative estimate of sampling quality
- Bring sampling within similar QC to analysis
- Tool to improving quality
  - Validate sampling protocol (with CTS)
  - Train and certify samplers (with SPT)

Conclusions (1)

• Sampling needs to be considered as first step in measurement process
• Uncertainty of Measurement needs to include contributions from all sources – including sampling (and physical sample preparation)
• Several approaches to estimating uncertainty – many explained later in Workshop
  - Each approach has particular strengths and weakness – different costs/feasibility
  - Select the approach best suited to measurement system under study
  - This aims to be a methodology applicable to a wide range of media (soil, water, food….)
• Estimates of U always have their own U on U – estimation is area of current research


*discussed by Katy Boon at 14:00
Conclusions (2)

• Values of U can be used to:
  • Improve the reliability of management decisions (e.g. compliance)
  • Judge FFP of measurements and
    - Validate the whole measurement method
  • Form rational basis for allocation of finance
    - for whole measurement, and between analysis and sampling
  • Provide tool for monitoring Quality of Sampling
• Value of U from initial validation might not be applicable to subsequent batches
• Sampling (and analytical) QC needed to monitor possible changes in U
  - Explained in later presentations
  - Full details in Guides (Eurachem and Nordtest)

Acknowledgements

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