Overview of Uncertainty from Sampling and the UfS Guide

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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*

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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 <u>all</u> steps in measurement (e.g. sampling)
- Key parameter of measurement (and sampling) quality
- *Doesn't assume measurements (or sampling) are correct*

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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 and QC processes

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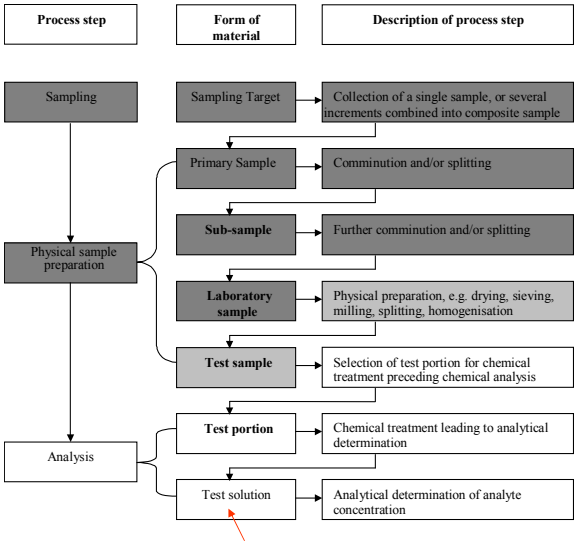
Sampling as part of the measurement process



More careful use of the word 'sample'

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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, 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 ± 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*
    - *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)*
      - (Kurfurst *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*

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Examples of estimating uncertainty of measurement *(including sampling)*

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

2 further examples in Nordtest Guide i.e.

Fe in iron ore - empirical

Conductivity in wastewater - empirical (variography)

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Statistical model
for ***Empirical*** estimation of uncertainty

$$x = X_{true} + \varepsilon_{sampling} + \varepsilon_{analytical}$$

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

X_{true} = *true* value of the analyte concentration in the sampling target

$\varepsilon_{sampling} + \varepsilon_{analytical}$ = effects on measured concentration from sampling and analysis

variance of measurement = $s^2_{meas} = s^2_{sampling} + s^2_{analytical}$

- includes between-organisational effects (e.g. sampling & analytical bias)

standard uncertainty = $u = s_{meas}$

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Four empirical methods for estimating uncertainty
including that from sampling

Method #	Method description	Samplers (People)	Protocols	Component estimated			
				Sampling Precision	Sampling Bias	Anal. Precision	Anal. Bias
1	Duplicates	single	single	Yes	No	Yes	No[1]
2	Multiple protocols	single	multiple	between protocols		Yes	No [1]
3	CTS	multiple	single	between samplers		Yes	Yes [2]
4	SPT	multiple	multiple	between protocols +between samplers		Yes	Yes [2]

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 where multiple labs involved

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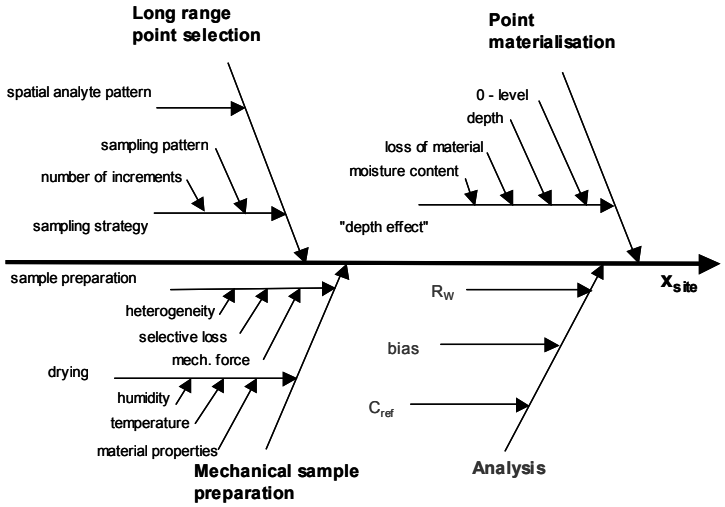
Budget Modelling Approach
to estimating U – ***Cause & effect diagram***



R_w is within-laboratory reproducibility

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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

$$\bar{x}_{site} = \bar{x}_{anal} \times f_{b-loc} \times f_{strat} \times f_{depth} \times f_{prep} \times f_{dry}$$

- $\bar{x}_{site}$ = measurement result
- $\bar{x}_{anal}$ = mean from the analysis of test samples
- $f_{\text{b-loc}}$ = 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

$$u_{\text{site}} = \sqrt{u^2_{\text{anly}} + u^2_{\text{b-loc}} + u^2_{\text{strat}} + u^2_{\text{depth}} + u^2_{\text{prep}} + u^2_{\text{dry}}}$$

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:-

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

$\sigma_r = \frac{\sigma_a}{a_L}$ = Relative standard deviation of the fundamental sampling error

σ_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

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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

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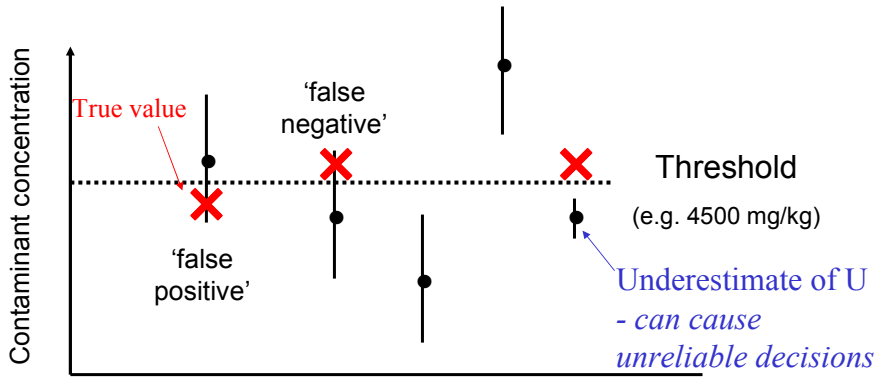
Know the U → make more reliable decisions



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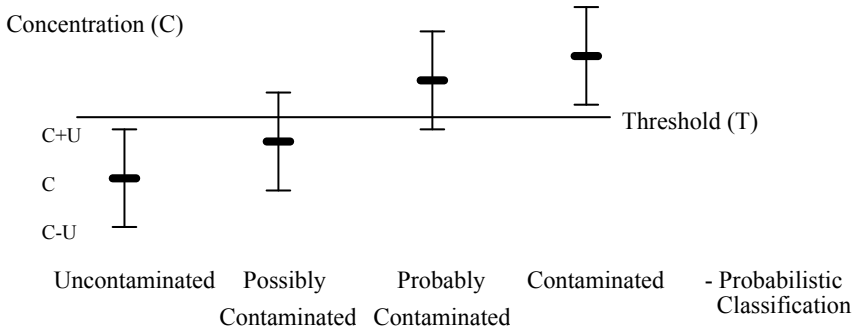
Effect of U on interpretation



How does this effect decisions on nitrate lettuce against threshold of 4500 mg kg^{-1} from Example A1 ?

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Effect of U on interpretation

SAMPLE TARGET	S1A1	Uncertainty	x - U	x + U	Probabilistic Classification
A	3898	639.3	3259	4537	Poss Cont
B	3910	641.2	3269	4551	Poss Cont
C	5708	936.1	4772	6644	Cont
D	5028	824.6	4203	5853	Prob Cont
E	4640	761	3879	5401	Prob Cont
F	5182	849.8	4332	6032	Prob Cont
G	3028	496.6	2531	3525	Uncont.
H	3966	650.4	3316	4616	Poss Cont

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

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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

* Lyn, J.A., Ramsey, M.H., and Wood, R. (2002) Analyst, 127, 1252 – 1260
based upon Thompson, M. and Fearn, T (1996), Analyst, 121, 275

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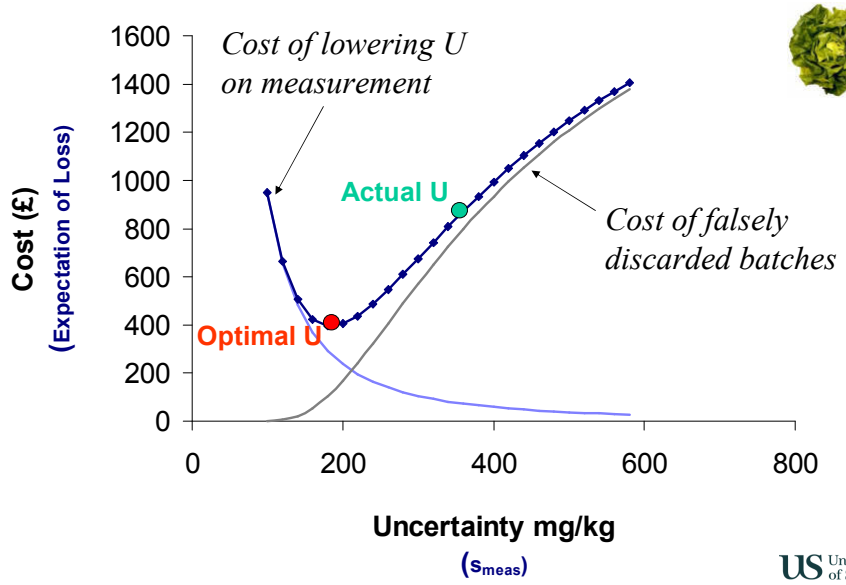
Acceptable level of Uncertainty?



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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 (= 2^2)
- 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

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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)

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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 UonU – estimation is area of current research

•Lyn, J.A., et al., (2007) The duplicate method of uncertainty estimation: are eight targets enough? Analyst 132, 1147-1152 (DOI: 10.1039/b702691a)

•discussed by Katy Boon at 14:00

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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)*

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Acknowledgements

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