Uncertainty from sampling soil: an empirical approach

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Presentation outline

- Uncertainty associated with the measurement of contamination in soil including sampling.
- The empirical approach to the estimation of sampling uncertainty
  - the Duplicate Method
- Case Study: demonstration of the Duplicate Method for the estimation of sampling uncertainty (Guide Example A2)
- Discussion
- Conclusions

Uncertainty in sampling in soil: where from?

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Sampling	Sample Preparation	Analysis
• the sampling protocol selected and its implementation. • the sampler • the sampling device • cross-contamination • small-scale heterogeneity • sample handling • the environmental conditions	• Drying • Storage • Grinding of the sample • Mixing of the sample • Dividing the sample	• in-lab **sub-sampling** • sample effects (e.g. matrix effects) • environmental conditions • storage duration and conditions, • instrument effects • calibration error, • operator effects

Uncertainty in sampling in soil: why measure it?

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- The use of concentration measurements:
  - comparison to regulatory thresholds
  - as the basis for reliable risk assessment
- At majority of sites it is the sampling that is the dominant source of uncertainty
- Important to quantifying the sampling uncertainty → confidence in the decisions made based on measurements taken

The estimation of uncertainty: an empirical approach

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- Determines directly the combined contribution to the uncertainty of the result
  - from all the sources of uncertainty
  - using method performance data from in-house or inter-organisational measurement trials.
- Looks at the scatter of replicated measurements
- Can then be broken down into contributions from components such as sampling and analysis (if required).
- Includes both systematic and random components (¹ precision of a method).

The 4 empirical methods for the estimation of measurement uncertainty

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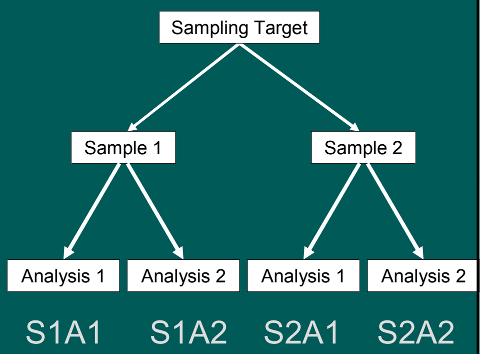
Method	Description	Number of samplers	Number of protcols	Components estimated			
				P_{anal}	B_{anal}	P_{samp}	B_{samp}
1	Duplicate samples	1	1	Yes	CRM	Yes	No
2	Different protocols	1	Multiple	Yes	CRM	Between protocols	
3	Collaborative Trial in sampling (CTS)	Multiple	1	Yes	CRM	Between samplers	
4	Sampling Proficiency Test (SPT)	Multiple	Multiple	Yes	CRM	Between protocols and between samplers	

The estimation of uncertainty: The Duplicate Method

- Random component
  - estimated from the precision of methods (sampling and analytical)
  - using the Duplicate Method and ANOVA or the range method (Example A3 in the guide)
  - both sampling and analytical uncertainty components.
- Systematic component
  - estimated from the bias of a method
  - use of CRMs to estimate the analytical uncertainty
  - only possible to estimate the sampling bias if have a Reference Sampling Target (RST) or by carrying out a CTS or SPT

The Duplicate Method: for the estimation of sampling uncertainty

- Define your sampling target and sampling protocol
- The duplicate method: using a balanced design …
  - Take a sample at the nominal sampling target.
  - Take a second sample displaced from the original to reflect the ambiguity in the sampling protocol
  - Carry out duplicate analyses on both the sample duplicates



- Repeat at 10 % of targets ($n \geq 8$)

The Duplicate Method: why n≥8?

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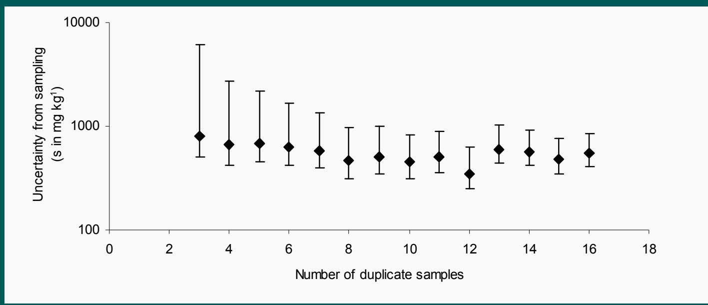
- n < 8 uncertainty of the uncertainty estimate is considered unacceptable.
- Above 3 the confidence interval on the uncertainty does improve (i.e. reduce) as the number of duplicates increases but to a progressively smaller extent ≥ 8.



The duplicate method: examples of how to take the duplicate sample

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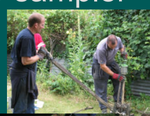
- When the sampling target is a specified depth interval e.g. 0 – 0.5 m, 0.5 – 1 m etc. of a core taken using a window sampler
  - the original borehole is located (e.g. with GPS), excavated with the window sampler and the original primary sample taken at the specified depth interval



  - the duplicate sample is taken from the same nominal depth interval from a duplicate borehole displaced from the original by a distance representative of the distance that represents the uncertainty of locating the original sample location

The duplicate method: examples of how to take the duplicate sample

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- When the sampling target is the volume of soil excavated from a trial pit to represent a 0.5 m depth interval
  - if the original sample is taken from one side of pile then the duplicate sample should be taken from the other side of the pile.

- Another example is presented in the Case Study which is discussed later.

Analysis of Variance (ANOVA)

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- ANOVA is used to estimate and separate the sampling and analytical components of measurement variance using the data produced by the Duplicate Method.
- Robust ANOVA (RANOVA) can be used accommodates up to 10% of population outliers.
- RANOVA can be carried out using ROBAN v1.01 based on AMC (1989) and Ramsey (1998).
- The Range method can also be used, an example is presented in the Guide (A3).

Case study: demonstration of the Duplicate Method for the estimation of sampling uncertainty

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The scenario:

- A former landfill, in West London
- 9 hectare = 90 000 m^2
- Potential housing development
- Key contaminant → Pb

The target:

- 30 m x 30 m area → depth of 0.15 m
- 100 sampling targets in total
  - ❖ A clear definition of the target is important

Case Study: the sampling protocol

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- a regular sampling grid, d = 30 m → 100 sampling locations
- top soil samples (0 – 150 mm)
- 100 primary samples
  - each intended to represent the 30 m x 30 m target
- samples collected using a sampling auger

- survey laid out with measuring tape and compass

Case Study:
the study design – duplicate method

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- duplicate samples taken at 10 sampling locations (i.e. 10%) randomly selected.
- 3 m from the original in a random direction
- this aims to reflect
  - the ambiguity in the sampling protocol
  - the uncertainty in locating the sampling target (e.g. survey error)
  - the effect of small-scale heterogeneity on the measured concentration within the sampling target

Case Study:
sample prep and analysis in the lab

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- Laboratory sample
  - oven dried, disaggregated and sieved (<2 mm)
  - ground (<100 μm) and mixed
- Test sample
  - 0.25 g sub-sample taken
  - where duplicate samples take a second 0.25 g (analytical duplicates – balanced design)
- Test portion
  - dissolution with nitric and perchloric acids
- Test solution
  - ICP AES determination of Pb

Case Study: sample prep and analysis in the lab

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- 6 soil CRMs were selected for analysis to assess the analytical bias over a range of concentrations
- Measurements subject to full AQC
- Corrected for reagent blank concentrations where statistically different to zero
- The raw measurements for use for the estimation of uncertainty were:
  - untruncated – e.g. 0.0124 mg/kg <u>not</u> < 0.1 mg/kg or < detection limit
  - unrounded – e.g. 2.64862 mg/kg <u>not</u> 3 mg/kg

Case Study: The results

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Row	A	B	C	D	E	F	G	H	I	J
1	474	287	250	338	212	458	713	125	77	168
2	378	3590	260	152	197	711	165	69	206	126
3	327	197	240	159	327	264	105	137	131	102
4	787	207	197	87	254	1840	78	102	71	107
5	395	165	188	344	314	302	284	89	87	83
6	453	371	155	462	258	245	237	173	152	83
7	72	470	194	83	162	441	199	326	290	164
8	71	101	108	521	218	327	540	132	258	246
9	72	188	104	463	482	228	135	285	181	146
10	89	366	495	779	60	206	56	135	137	149

30 m

- Only 16/100 locations over UK SGV = 450 mg Pb/kg
- Mainly uncontaminated (84%)

Argyraki (1997)

Case Study: The results – from the balanced design

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- Low level agreement between sample duplicates (e.g. D9) → high level of sampling uncertainty

- Agreement between analytical duplicates much better < 10 % difference

SAMPLE I.D.	S1A1 (mg kg^{-1})	S1A2 (mg kg^{-1})	S2A1 (mg kg^{-1})	S2A2 (mg kg^{-1})
A4	787	769	811	780
B7	338	327	651	563
C1	289	297	211	204
D9	662	702	238	246
E8	229	215	208	218
F7	346	374	525	520
G7	324	321	77	73
H5	56	61	116	120
I9	189	189	176	168
J5	61	61	91	119

- Robust ANOVA (Roban) selected to allow for the outlying values evident in this data.

Case Study: Roban output

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Geochemical = between-target

unit = mg kg^{-1}

CLASSICAL ANOVA RESULTS

Mean = 317.79999

Standard Deviation (Total) = 240.19238

Sums of Squares = 1738031.9 370075.5 6473

	Geochemical	Sampling	Analysis
Standard Deviation	197.55196	135.43246	17.990274
Percentage Variance	67.646327	31.792678	0.5609926

ROBUST ANOVA RESULTS:

Mean = 297.30884

Standard Deviation (Total) = 218.48763

	Geochemical	Sampling	Analysis	Measurement
Standard Deviation	179.67409	123.81386	11.144044	124.31436
Percentage Variance	67.62655	32.113293	0.26015487	32.373447
Relative Uncertainty (% at 95% confidence)	-	83.289726	7.4966113	83.626415

Case study:
The uncertainty estimates

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- The estimates of the random component of the measurement uncertainty are averaged over the 10 targets (= 10 %, n ≥ 8)
- Assuming that the uncertainty is not varying significantly over this range of concentration
- Expressed in relative terms to be applicable to full range of values

Case study:
Random component

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s_{samp} = 123.8 mg kg^{-1} and s_{anal} = 11.1 mg kg^{-1}

added together by their squares to give the random component of the combined standard deviation of measurements:

$$s_{meas} = \sqrt{(s_{samp}^2 + s_{anal}^2)} = 124.3 \text{ mg kg}^{-1}$$

multiplied by a coverage factor (k = 2 for 95% confidence) to estimate the random component of the standard uncertainty:

$$u = k.s_{meas} = 248.6 \text{ mg kg}^{-1} \text{ (for a single sample)}$$

Case study: Random component

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This can also be expressed as a relative expanded uncertainty:

$$U_{meas}' = \frac{200 . s_{meas}}{\bar{x}} = 83.63\ \%\ \text{(of the concentration values)} \approx 84\ \%$$

For sampling alone:

$$U_{samp}' = \frac{200 . s_{aamp}}{\bar{x}} = 83.29\ \%\ \text{(of the concentration values)}$$

For analysis:

$$U_{anal}' = \frac{200 . s_{anal}}{\bar{x}} = 7.47\ \%\ \text{(of the concentration values)}$$

Case Study: sources of uncertainty

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- Proportion of U caused by **sampling** (123.8 mg kg-1)

$$= 100 \times \frac{s_{samp}^2}{s_{meas}^2} = 100 \times \frac{123.8^2}{124.3^2} = \underline{99.2\%}$$

Dominant source of uncertainty

- Proportion of U caused by **analysis** (11.1 mg kg-1)

$$= 100 \times \frac{s_{anal}^2}{s_{meas}^2} = 100 \times \frac{11.14^2}{124.3^2} = \underline{0.8\%}$$

Case Study: inclusion of analytical bias

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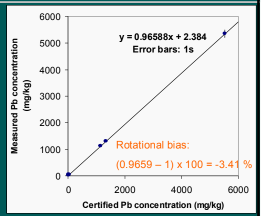

- A linear functional relationship was fitted between the measured values and the certified values of the 6 CRMs using FREML to model the analytical bias:
  - 3.41 % ± 1.34 %
- The systematic component of the relative expanded uncertainty:

$$U_{systematic}' = 2.\sqrt{(-3.41^2 + 1.34^2)} = 7.33\ \%$$

- Currently no consensus on how to combine the systematic and random components of uncertainty, one method is to add them by the sum of their squares:

$$U_{total}' = \sqrt{(U_{random}^2 + U_{systematic}^2)} = \sqrt{(83.63^2 + 7.33^2)} = 83.95\ \% \approx 84\ \%$$

Case Study: Probabilistic classification

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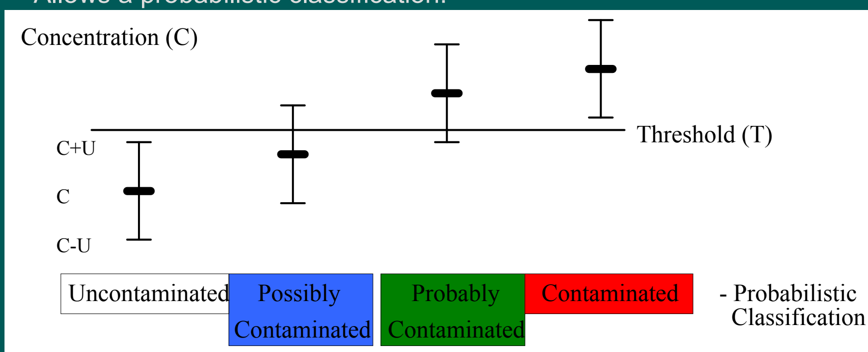
- Should always report the uncertainty values with the analyte concentration value as it can alter the classification of the sampling location.
- Allows a probabilistic classification:



Case Study:
Probabilistic classification

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9	72	188	104	463	482	228	135	285	181	146
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41% of locations at least 'possibly contaminated'

Discussion:
Sampling bias

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- This estimate of sampling uncertainty (and measurement uncertainty) from the Duplicate Method does not take into account the sampling bias.
- But as it is the heterogeneity of the sampling target that is the dominant source of uncertainty, it is assumed that the contribution to the uncertainty of the sampling bias is inconsequential by comparison.
- Possible to include an estimate of the contribution from sampling bias, if use one of the methods involving multiple protocols or samplers (e.g. CTS and SPT)

Discussion: U at duplicate locations

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- At targets where duplicate samples have been taken the uncertainty on these locations is reduced as 4 measurements have been taken as part of the Duplicate Method and the mean of these measurements is used to represent the concentration at that location, i.e. a composite with an increased sample mass.
- The uncertainty at these locations can be estimated from:

$$\frac{s_{meas}}{\sqrt{4}}$$

- In the case study the uncertainty at the targets where duplicates were taken is: $\frac{84}{\sqrt{4}} = 42\ \%$

Discussion: if the site mean is the measurand

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- If the whole site is defined as the sampling target
  - and the measurand (or true value) had been defined as the mean concentration across the whole site
- The uncertainty estimate could consist of the standard error on the mean
- In this case study:
  - s_{total} = 403 mg kg^{-1}, $\bar{x}$ = 291.9, n = 100
  - sem = $\frac{s_{total}}{\sqrt{n}} = \frac{403}{\sqrt{100}}$ = 40.3 mg kg^{-1}
  - the relative expanded uncertainty on the mean is:

$$= 200\,\frac{sem}{\bar{x}} = 200 \times \frac{40.3}{291.9} = 27.6\ \%\text{ of the mean value}$$

- But …
  - ignored systematic effects (underestimates U)
  - don't get the components

Conclusions

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- Importance of estimating the measurement uncertainty and in particular including that from sampling.
- Clear definition of the target required.
- The simple application of the Duplicate Method for the estimation of the sampling uncertainty
- How the the duplicate samples are taken is important
- The usefulness of ROBAN and robust ANOVA as a tool for the estimation of measurement uncertainty and the separation of the sampling and analytical components for populations with < 10 % outliers.

Conclusions

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- 84 % for single sample protocol
- If 84 % not fit-for-purpose might need to reduce U_{meas} (Thompson and Fearn (1996) and Taylor et al (2002))
  - FFP assessment showed that an optimal U_{meas} would be 28%, this would require a ~ 3 - fold reduction in the uncertainty.
  - As sampling usually dominates U_{meas} it is possible to reduce the U_{meas} by increasing the sample mass by taking a composite sample.
    - An increase in sample mass of a factor of n would reduce the sampling uncertainty by a factor of $\sqrt{n}$ (i.e. a 9-fold composite would in theory reduce the uncertainty by 3)
- Estimates of U are not automatically applicable to other sites
  - Need a QC approach over repeated sites

Conclusions

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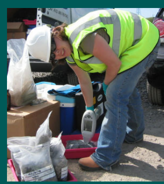
- This technique has also been shown to be applicable to:
  - other analytes
  - other media
    - food (Example A1 in the Uncertainty from Sampling Guide)
    - gas (Squire and Ramsey, 2001)
    - river sediment (Ramsey *et al*, 1992)
  - on site measurement techniques
    - Argyraki *et al* (1997) and Taylor *et al* (2004)
    - current work on the increased acceptability of on-site measurement tools



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