# *The way forward for Uncertainty from Sampling*

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Uncertainty from sampling and analysis for accredited laboratories
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## Overview

- New applications of existing UfS estimation methods
  - *In situ* – at mm scale (PXRF), and µm scale (SIMS) – sensors in general
    - Passive – ϒ-ray Spec
  - On site – briefly mentioned here
- Need to further develop methods for estimation of UfS
- Gaining benefits from knowing UfS
  - E.g. improving sampling to reduce UfS to achieve FFP
- External factors affecting take up of UfS estimation
  - Management of the whole measurement process
- Conclusions

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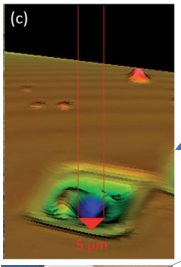
## UfS estimation for a wider range of measurement types
## *In situ* measurements in general




- Taken *in situ* without disturbing or removing the test material
  - Sampling indivisible part of measurement process, e.g.
  - Soils - handheld portable (P)XRF for some metals
  - Minerals – SIMS at micron scale
  - Gases - many sensors – how most measurements are made!
    - e.g. Photolonisation detectors for VOCs, (e.g. benzene), IR for $CH_4$, $CO_2$
  - Liquids - e.g. pH, UV-Vis for $NO_3$, TOC, $H_2S$
  - Clinical - Transcutaneous Bilirubinometer (TcB) – jaundice ?
- Less expensive than traditional *ex situ*, so
  - more measurements can be taken
  - giving better coverage of target in space and/or time
    - Even 100% coverage – e.g. groundhog ($\gamma$–ray spec)
- Measurements often have larger uncertainty
  - due partially to heterogeneity of analyte concentration (not mixed)
  - detection limits often not as low as for *ex situ* measurements
  - U can be estimated by duplicate method (or SPT)
  - can be shown fit-for-purpose if UfS quantified (example follows)



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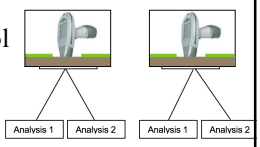
## UfS estimation for *in situ* measurements

- 'Sample duplicate' = duplicated positioning of probe, using same sampling protocol
- 'Analytical duplicate' from duplicated measurements made without moving probe




- Systematic component of uncertainty (from bias)
  - can't be estimated only with matrix-matched CRMs, as:-

| CRM | Dried | Ground | Homogeneized | Compacted |
|---|---|---|---|---|
| Test material | Moist | Unground | Heterogeneous | Un-consolidated |


- Comparison required, between measurements made *in situ* and those made *ex situ*,
  - ideally with independent analytical method for same measurand
  - on samples taken from same sampling target
- Explain with Example

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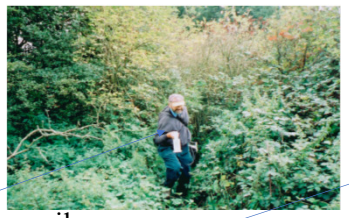
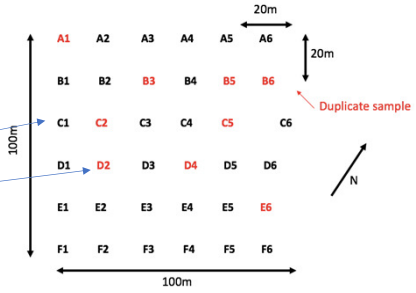
# UfS estimation for *In situ* measurements (at 5mm scale)



- Nature reserve -**West London**
- Ex-Firing range
- Measurements of Pb concentration in topsoil.
- Compare *in situ* PXRF against traditional field sampling
  - with *ex situ* lab (AAS) measurements
- 100 x100m site – 36 sampling targets
- UfS estimated with duplicate method
  - balanced design
  - at 9 sampling targets
- Bias against 6 CRMs, -11% for PXRF, -1% for AAS




Taylor P D, Ramsey M H and Potts P.J. (2004) Balancing measurement uncertainty against financial benefits: a comparison of *in situ* and *ex situ* analysis of contaminated land. Environmental Science and Technology 38, 6824-6831

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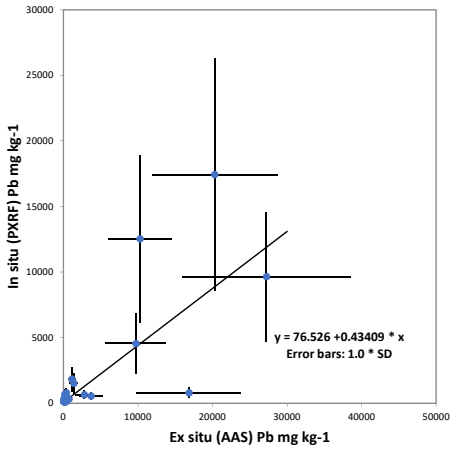
# 'Bias' between *in situ* and *ex situ*
## = systematic component of UfS – *using FREML*




- Model relationship using FREML* (n =35)
  - Allows for uncertainty on BOTH axes
- Model: In situ Pb = 0.43 (± 0.08) x Ex situ Pb + 77 (± 26)
- **'Bias' = -57%**
  - caused by soil moisture, material >2mm, surface roughness, and depth difference
- Debate about whether to (1) 'correct' *in situ* to agree with *ex situ* measurements (or *vice versa*)
  - Perhaps *in situ*[Pb] is closer to true value being experienced by living organisms*
  - Depends on definition of measurand
- Or (2) include 'bias' in estimate of U
- *Needs further research*

*Functional Relationship Estimation by Maximum Likelihood, AMC Technical Brief Number 10 (2002), software from:- https://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/

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# UfS estimation of *in situ* measurements & FFP

- Random component of UfS calculated using RANOVA of duplicate measurements -

| parameter | *Ex situ* | *In situ* |
|---|---|---|
| | [Pb] mg $kg^{-1}$ | |
| Robust mean | 749 | 1045 |
| $s_{analytical}$ | 14 | 61 |
| $s_{sampling}$ | 310 | 529 |
| $s_{meas}$ | 311 | 532 |
| U' | 83% | 102% |

*In situ* Analysis gives higher U – but not dominant source

Sampling is dominant sources of U (>99% in both cases)

  - Uncertainty Factor would probably have been better than U'– not around then
- One Benefit of knowing UfS is the ability to judge fitness-for-purpose, described in:-
  - UfS Guide Section 16 of, applied here using Optimized Uncertainty method = OCLI
  - OCLI method in ISO 18400-104:2018, Soil Quality – Sampling – Part 104: Strategies, Annex C
  - i.e. was the sampling (and analysis) good enough?

Taylor P D, Ramsey M H and Potts P.J. (2004) Balancing measurement uncertainty against financial benefits: a comparison of *in situ* and *ex situ* analysis of contaminated land. Environmental Science and Technology 38, 6824-6831

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# Judging FFP using Optimized Uncertainty (OCLI) equation

$$E(L) = C\,[1 - \Phi\,(\varepsilon_1 / s_{meas})\,] + D/s^2_{meas}$$

E (L) – expectation of financial loss

$s_{meas}$ – measurement uncertainty

Φ – standard normal cumulative distribution function

ε1 – error limit = $|\,T - c\,|$

(T = threshold value, c = contaminant concentration)

D – combined optimal cost for sampling and analysis

C – consequence costs (e.g. potential losses resulting from misclassification)

| | Cost per measurement (£) | | Consequence cost of misclassification | |
|---|---|---|---|---|
| | $L_{samp}$ | $L_{anal}$ | C(remediation) | C(legal) |
| Ex situ (AAS) | 10 | 10 | 42000 | 10000 |
| In situ (PXRF) | | 13 | 10500 | 10000 |

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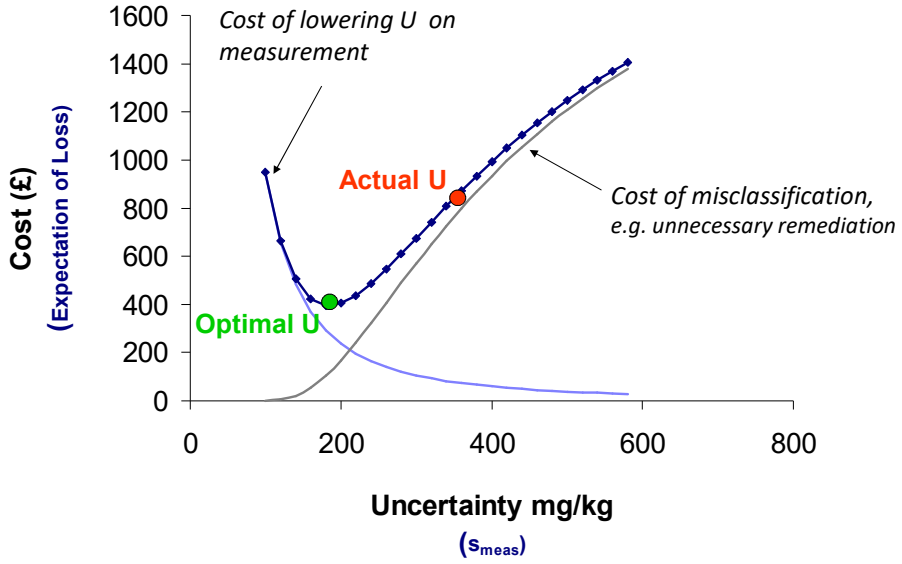
## Judging FFP – at Acceptable level of Uncertainty?

General Case

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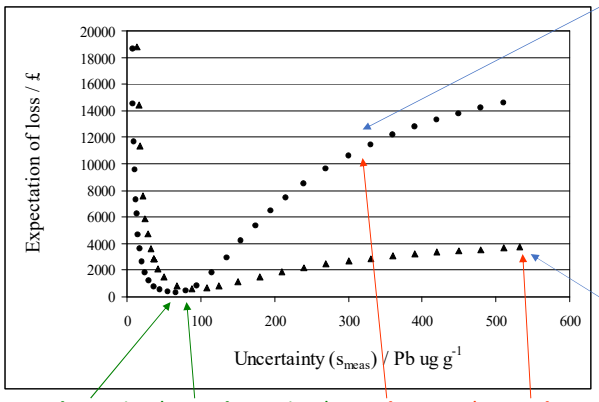
## Is *in situ* or *ex situ* more cost effective?

For Case Study

Neither *in situ* or *ex situ* procedure is currently Fitness-for- Purpose (FFP)




Both *in situ* (●) and *ex situ* (▲) have far larger $U_{meas}$ (x 5) than is optimal to achieve FFP

Reduction of UfS needs use of composite measurements within each target

4-fold Composite measurement should lower UfS x 2, & reduce cost by~ x2 Using model ($s^2 \propto 1/m$)

*In situ* has generally lower overall cost (x3) without improvement

| ***Ex situ*** optimal uncertainty | ***In situ*** optimal uncertainty | ***Ex situ*** actual uncertainty | ***In situ*** actual uncertainty |
|---|---|---|---|
| 68 ug $g^{-1}$ | 88 ug $g^{-1}$ | 311 ug $g^{-1}$ | 532 ug $g^{-1}$ |
| | | **£11,000** | **£3,700** |

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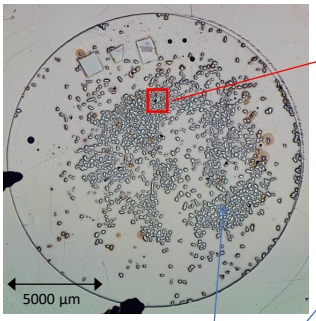
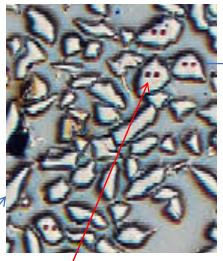
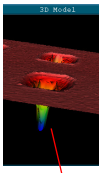
# Duplicate Method at micron scale on *in situ*

## Estimation of UfS and $U_{heterogeneity}$ for SIMS measurements





**Fragments of NBS 28 Glass**
- Mean diameter ~ 230µm

Mass estimated as ~ 20µg
Select 100 sample fragments
Use **Duplicate method** to estimate U

**Duplicate measurements**
- 50 µm apart
- **made on each of 100 fragments**
- measure at different times in run
- **run over 15 hours**

Sample mass from crater
- ~ 300-350 pg

**$^{18}O/^{16}O$ in NBS 28 Glass CRM**

Helmholtz Zentrum, Potsdam, Germany

SIMS = Secondary Ion Mass Spectrometry

Ramsey MH and Wiedenbeck M. (2017) Geostandards and Geoanalytical Research, 42,1,5-24

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# Uncertainty estimates for NBS28 at micron scale

- Use ANOVA to estimate Uncertainty
- expressed U in units of 'per mil' ‰ $= 1000 * s / \bar{x}$
  - Unit widely used in isotopic analysis for repeatability and heterogeneity,

Summary of Uncertainty estimates for NBS28

| | Total | **Between-dups** | **Within-dups** | Num pairs |
|---|---|---|---|---|
| Uncertainty 1s(‰)* | 0.31 | **0.28** | **0.14** | 97 |

- $U_{anal}$ = Analytical repeatability estimated from 'within-duplicate' = **0.14‰**
- $U_{samp}$ = between-fragments from Heterogeneity ($U_{het}$) quantified as **0.28 ‰**
  - adds to $u_{analyical}$ to give total repeatability/$U_{meas}$ of 0.31‰
  - dominates total measurement variance ($U_{samp}$ contributes 81%)

- Full measurement uncertainty estimate would require bias against matched CRMs & between-lab variance

Ramsey MH and Wiedenbeck M. (2017) Geostandards and Geoanalytical Research, 42,1,5-24

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# UfS of passive *in situ* measurements of radioactive decay

## Case Study: $^{137}$Cs in soil at Dounreay


- Area within nuclear decommissioning site
  - $^{137}$Cs measured with $\gamma$-ray spectrometry (both *in situ* and *ex situ*)
- Objectives - **Comparison of *in situ* against *ex situ* surveys**

P Rostron, J A Heathcote, M H Ramsey (2015) Evaluation of uncertainties in *in situ* and ex situ gamma measurements on land areas with low contamination levels. *Journal of Radiological Protection* 35 (2015) 391-399.

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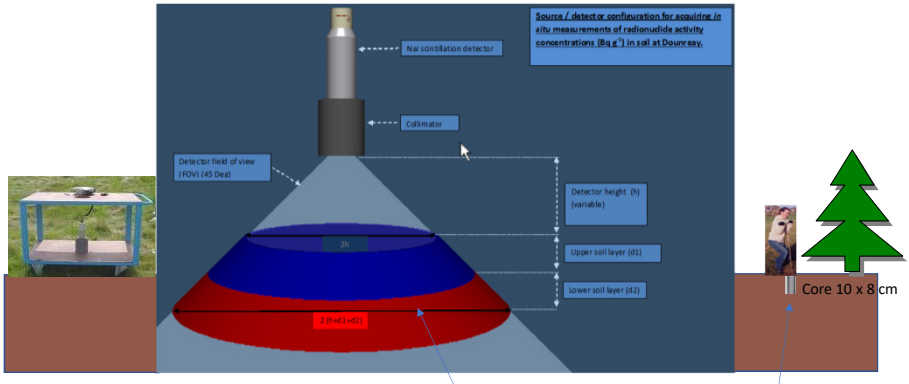
# *In situ* measurements by $\gamma$-ray spectrometry




- *In situ* NaI detector responds to $\gamma$-rays (e.g. from decay of $^{137}$Cs)
- Mass of soil 'sample' 200 -**1000 kg**
- ~1000 larger mass than physically extracted (e.g. **~ 0.5 kg**)
  - for *ex situ* measurement by $\gamma$-ray spec.

Rostron P., Heathcote J. and Ramsey, M.H. (2015) Making best use of *in situ* gamma measurements in radioactively contaminated land investigations. Nuclear Future Volume 11, Issue 1, 56-60, January 2015

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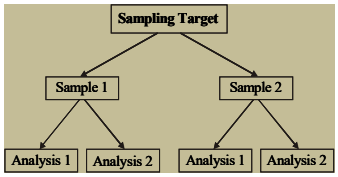
# Measurement Uncertainty at individual sampling targets

U estimated using *duplicate method*.

Sampling and analytical duplicates at 8 sampling targets for *ex situ,* & 12 for *in situ*




Sampling and analytical uncertainty using robust ANOVA.

| | $U'_{anal}$% | $U'_{samp}$% | $U'_{meas}$ % |
|---|---|---|---|
| *Ex situ* | 5.1 | 72.5 | 72.6 |
| *In situ* | 7.5 | 10.2 | 12.6 |

- $U'_{analytical}$ greater for *in situ* - Shorter counting time, environmental conditions.
- $U'_{sampling}$ much greater for *ex situ* - Effect of very small sample mass + heterogeneity.
- Combined $U'_{measurement}$ greatest for *ex situ* - exceeds *in situ* by factor of 6 in this area.
  - Bias in measurements could also be included in U, but no CRM was available
  - No significant bias found between measurements made *in situ* and *ex situ*

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# UfS estimation for On site measurements

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- 'On site' measurements - when a sample taken from original location, usually prepared and homogenised, measured close to its original location.
- Situation is intermediate in complexity between traditional *ex situ* measurements, and *in situ* measurements

Example: Determination of total petrol hydrocarbons (TPH) in stockpiled soil*

- *ex situ* measurement made by on-site method
  - SiteLAB_UVF 3100 fluorescence spectrometer
- compared against those made in remote laboratory (GC-FID, with more QC)
- Duplicate method applied to both methods in usual way (+CRMs for bias)
  - on site [TPH] 3 x higher than off site measurement, maybe due to:-
  - loss of volatile TPH in samples taken off site
  - differences between the definitions of measurand for the two TPH analytical methods

*K A Boon and M H Ramsey (2012) Judging the fitness of on-site measurements by their uncertainty, including the contribution from sampling. *Science of the Total Environment* 419, 196–207 http://dx.doi.org/10.1016/j.scitotenv.2011.12.001

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**Slide 16**

**MOU23** Ditch this slide - just put key points elsewhere (conclusions?)
Microsoft Office User, 07/11/2019

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# General directions for UfS estimation and reduction (1)

1. **Encourage use of Uncertainty Factor**
   - as a better way to express U in appropriate circumstances
2. Make available **Confidence Limits on estimates of UfS** (and heterogeneity)
   - Enables rigorous comparison of UfS values estimated by different methods and for different analytes
3. Improve ways of **Modifying UfS** in order to achieve Fitness-for-Purpose (FFP)
   - Why some systems behave in predictable ways ($s^2 \propto 1/m$), and others don't
   - Improve the modelling of UfS for such systems
4. Encourage and develop **Sampling QC** procedures (Section 13 of Guide) to check:
   - whether the conditions present at validation are still present
   - whether initial estimates of U are still applicable
     - Especially where subsequent targets very different (e.g. contaminated land)
     - Perhaps add in separate estimate of heterogeneity for each site?

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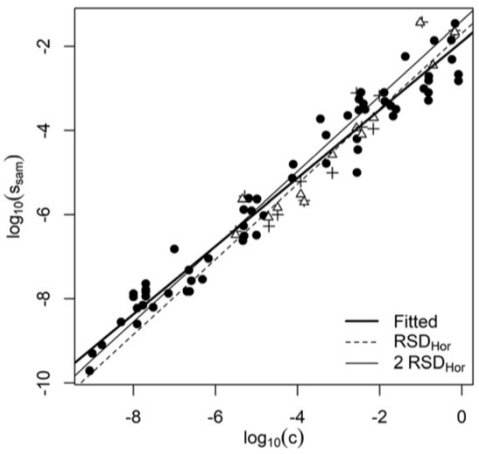
# General directions for UfS estimation and reduction (2)

5. Compile **databases of UfS**/UoM estimates <u>across a whole sector</u> to see:
   A. If there are typical values that could be used for prediction of UfS (e.g. by regulators)
      - As Ellison et al.(2017)*, did for **food sector**
      - ~ 27 different food products (from field/store/factory/retail)
      - ~75 different analytes
      - Found Horwitz-like relationship
      - provides estimate of UfS to within ~ an order of magnitude.

   B. Get more evidence to test whether UfS increases as a function of concentration <u>in other sectors</u>*




*Ellison, SLR, Ramsey MH, Lawrance P, Stuart B, Minguez J, Walker MJ, (2017) Is measurement uncertainty from sampling related to analyte concentration? Analytical Methods, **9**, 5989-5996. DOI: 10.1039/C7AY00752C. http://pubs.rsc.org/en/content/articlelanding/2017/ay/c7ay00752c#!divAbstract

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**Slide 17**

**MOU13** This slide is general wish list - move later? Or combine with later lists?
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# External factors affecting take up of UfS estimation

- Awareness of UfS - improve with 2019 UfS Guide etc.
- Regulatory and accreditation requirements to estimate UfS
  - improving with sampling in ISO/IEC 17025:2017 clause 7.6.1 to evaluate UfS
- Cost of estimating UfS
  - reduce cost of estimation with unbalanced or simple design
  - emphasise reduction in overall cost by avoiding adverse effects of UfS (e.g. loss of product)
- Including UfS in conformity assessment and compliance decisions
- – find better ways
  - e,g. Food sector currently excludes UfS
  - Assumes samples are 'representative', therefore UfS is 'zero'!
- Management of samplers/sampling process
  - need to integrate sampling into whole measurement process
    - Not administer sampling as a separate process
    - Educate samplers in the measurement process

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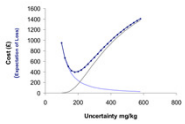
# Conclusions



- Increase range of sectors and situations where UfS is being estimated, e.g.
  - ***in situ*** measurements (e.g. sensors) makes UfS estimation more applicable
    - needs more development (e.g. correct for 'bias'?)
  - **Passive** measurements - *in situ* can be better than *ex situ*
    - due to much larger (x 1000) sample mass, and much lower cost (so better coverage)
  - at **micro-scale** (EPMA, SIMS, LA-ICPMS etc.)
  - for **heterogeneity** estimation (e.g. for $U_{HET}$ candidate CRMs)
  - Microbiology and other new sectors
- Realise benefits of knowing UfS, e.g.
  - Enables critical assessment of FFP of all sampling and analytical methods
  - measurements with higher U can be shown to be fit for some purposes
    - e.g. *In situ* and sensor measurements
- Encourage integrated management of field sampling as part of measurement process

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