Sampling Aspects of BS10175:2010 The central role of uncertainty to judge fitness-for-purpose of SI

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Overview

- Traditional view of Sampling & Analysis *separately*
- Benefits of integrated view of measurement process
- What is Uncertainty of Measurement (U)?
- Benefits of knowing U on every measurement
 e.g. judging Fitness For Purpose (FFP)
- Case studies show cost savings
- What needs to go into BSI 10175
- Conclusions



Traditional view of sampling & analysis

Sampling: – assume representative if you stick to the protocol

• 3.12 sampling

methods and techniques used to obtain a representative sample of the material under investigation

- Better definition *Process of drawing or constituting a sample*. ISO 11074-2 (1998)
- Estimate the uncertainty to see <u>how</u> representative sampling was

Analysis: assume measurements ≈ true values if accredited

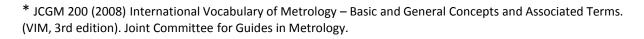
- Ignore the fact that all measurements are wrong
 - to some extent
- measurements all have uncertainty



What is Uncertainty of Measurement?

3.7 Measurement uncertainty

- parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the <u>measurement</u>
- Misquoted, should be 'attributed to the measurand'
 - = 'quantity intended to be measured'(JCGM 200, 2008)*.
 - ~ true value of contaminant concentration
- Older definition clearer:-
- 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)
- Sampling uncertainty: The part of the total measurement uncertainty attributable to sampling. IUPAC (2005)
- Analytical uncertainty: The part of the total measurement uncertainty attributable to chemical analysis.





Case Studies - 6 routine Site Investigations

Site	Area ha	Main type of contamination	Suspected source	Site end-use	Sampli ng method	Primary contaminant
1	8	Heavy metal	Tin mining	Housing	Trial pits	Arsenic
2	1.5	Organic	Infill waste from gas works	Recreational land	Trial pits	Indeno(123) pyrene
3	0.08	Heavy metal	Infill after WWII bombing	Garden and allotment	Window sampling	Lead
4	12	Organic	Gas works	Hazard assessment	Trial pits	Total PAH
5	45	Heavy metal	Railway sidings and colliery spoil	Nature reserve	Trial pits	Arsenic
6	1	Heavy metal	Ex-firing range	Housing	Hand auger	Lead

Wide range of different: - sites (size, history & value),

- contaminants, sampling methods

Taylor P.D., Ramsey M.H. and Boon K.A. (2007) Estimating and optimising measurement uncertainty in environmental monitoring: an example using six contrasting contaminated land investigations. Geostandards and Geoanalytical Research, 31, 237-249 Taylor P.D., Boon K.A. and Ramsey M.H. (2007) *Cost-effective investigation of contaminated land*, CL:AIRE report RP4, CLAIRE, London. ISBN 978-1-905046-01-0.



Estimation of uncertainty in a routine site investigation Site 4 - Gas Works, East London





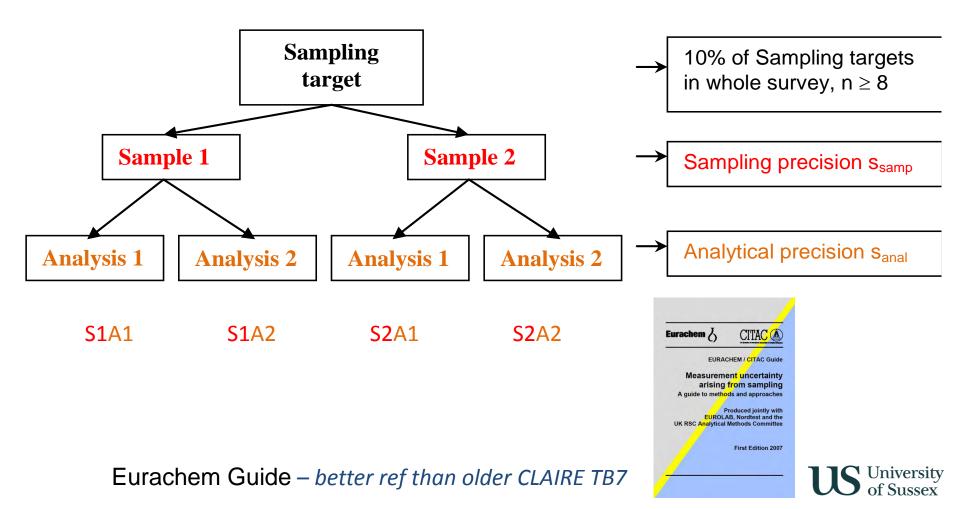
Site	Area ha	Main type of contamination	Suspected source	Site end-use	Sampli ng method	Primary contaminant
4	12	Organic	Gas works	Hazard assessment	Trial pits	Total PAH



Estimating U

using the Duplicate Method

(BS10175:2010 Annex D)



Duplicate Results at Gasworks Site

S1 A1	S1A2	S2 A1	S2A2

1	6.4	6.5	13.6	14.2
2	52.3	55.2	70.2	79.4
3	99.0	96.5	36.1	59.6
4	8.1	6.0	3.7	31.6
5	247.4	368.4	133.7	146.3
6	148.8	109.3	187.9	233.2
7	50.1	85.5	112.2	42.6
8	15.2	33.9	17.6	18.5

PAH (mean conc 76 mg/kg)	Standard Uncertainty (1s) mg/kg	Relative Expanded Uncertainty (2s) %	
Sampling (inc prep)	27	71%	
Analysis	20	53%	
Measurement	34	89%	

Much higher than quoted by lab - MCERTS 30%(2s) Precision



Estimates of Uncertainty

in 6 Case studies

Site number	Key contaminant	U'random (%)	U'meas (%)	% of measurement variance	
				Sampling	Analysis
1	Arsenic	63.7	66.7	85.6	14.4
2	Indeno(123- cd)pyrene	50.8	54.6	80.3	19.7
3	Lead	25.3	32.2	58.9	41.1
4	Total PAH	89.3	91.5	60.5	39.5
5	Arsenic	157.6	158.9	-	-
6	Lead	75.1	77.8	86.6	13.4

U' meas (including analytical bias) ranges from 32 – 159% (at 95% confidence)

Main source of U is in the sampling (60-90% of total U)

- is this level of U acceptable – are measurement fit-for-purpose?



Judging Fitness-For-Purpose (FFP)

using OCLI method.

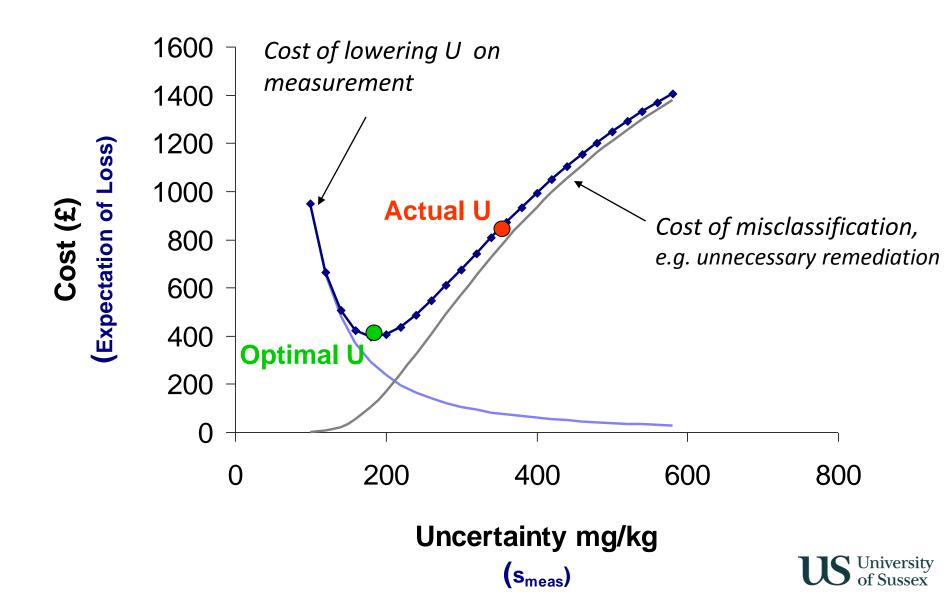
- Estimates the Fitness-for-purpose (FFP) of measurements overall,
 - corresponds to minimum cost (expectation of lost)
 - sub-divide to estimate FFP of analytical and sampling components separately.
- Considers
 - all costs of measurement,
 - potential cost of misclassification
 - e.g. end-use, unnecessary remediation, potential litigation.

• Details in Ramsey M.H., Taylor P. D. and Lee J.C. (2002) **Optimized Contaminated Land Investigation (OCLI)** at minimum overall cost to achieve fitness-for-purpose, Journal of Environmental Monitoring, 4, 5, 809 - 814

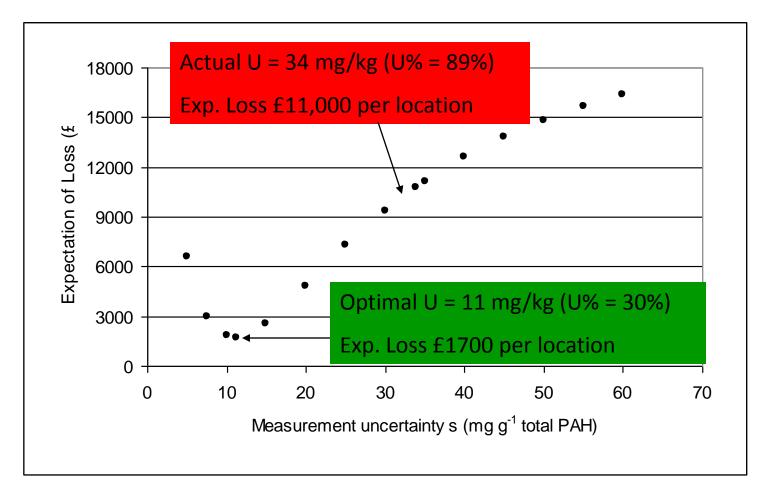




Acceptable level of Uncertainty?



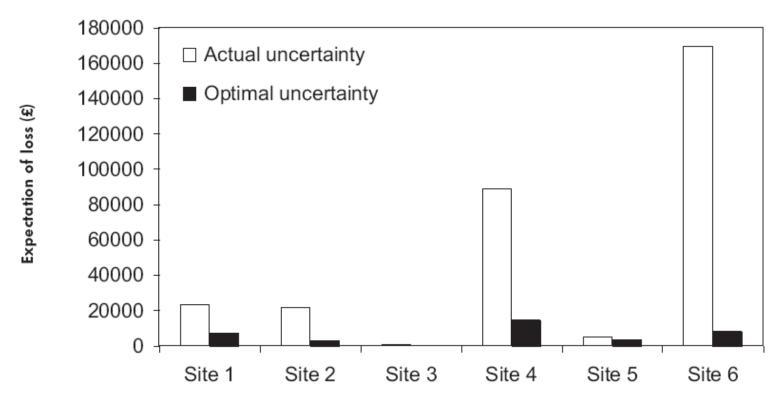
Actual v Optimal U for Gasworks Site



Overall saving of £74,400 on whole development



Financial Saving from optimal U



Expectation of financial loss estimated for whole sites for 6 routine site investigations.

Cost are calculated at either:- uncertainty actually found (clear bars), or optimal value (black bars) Site 6 has largest potential saving of £160,000

Reduce sampling uncertainty by taking composite samples (e.g. BS10175:2001)

e.g. 9-fold composite ('cluster') reduces U from Sampling by factor of $\sim \sqrt{9} = 3$



What needs to go into BSI 10175?

- Integrated view of measurement process
 - Sampling + Analysis
- Importance of realising all measurements are uncertain
- Need to report U value for all measurements (S&A)
- Enables:-
 - judgement of whether measurements are FFP
 - by investigator, user & regulator
 - Shows how to make measurements FFP (e.g. comp. samples)
 - Probabilistic interpretation of the site (e.g. EA, 2009)
- So:- 'Strongly recommend estimation of Uncertainty from sampling' (Sections: 5.7.1 Decision 4)



Estimating Uncertainty – Annex D

- Applies to field sampling (Sec 7.8 as QC?) sample prep & anal (Sec 9.3)
- When to 'Estimating sampling uncertainty using the duplicate method might be (is generally recommended but ?) particularly appropriate when':
 - a) the <u>confidence and robustness</u> required of decisions to be based on the information from the site investigation is <u>high</u>; ALWAYS?
 - b) an investigation involves a large number of sampling locations
 - NO just need 8 duplicates so a minimum of 8 samples (i.e >10% of locations) DELETE
 - c) the analytical results are close to the site assessment criteria;
 - if away from T show higher U (lower cost) justified
 - d) the ground is expected to be highly heterogeneous.
 - Common on contaminated site don't know otherwise without duplicate samples!

Explain practicality & utility - saving money on development overall, - judging and demonstrating fitness-for-purpose (FFP) (add to list)



Accepted in European Guidance – with contaminated land example*

- better to cite than earlier CLAIRE TB7
- also give design needed to quantify the contribution from sample preparation (Appendix D)

* Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide: *Measurement uncertainty arising from sampling: a guide to methods and approaches Eurachem* Ramsey M.H., and Ellison S. L. R.,(eds.) (2007) ISBN 978 0 948926 26 6. (http://www.eurachem.org/guides/UfS_2007.pdf)



What needs to go into BSI 10175?(2)

- Don't just consider UfS as part of QC = pass/fail give values of Uncertainty to user
- Composite samples Importance for reducing U.
 - Currently not recommended (7.6.2.6 Composite sampling and Table 9),
 - however 'cluster samples' = closely spaced incremental samples(8.3.2) 'may' be taken (e.g. for trial pits) to make samples 'representative'.
 - composite sample in international terminology just with increments taken over a smaller scale than envisaged for the not recommended 'composite' samples.
- Reasons for not taking composite samples (sec 7.6.2.6) can all be refuted if U known:-

a) difficulty of comparing resultant data with guideline concentrations that relate to spot samples;

- - just lower measurement uncertainty

b) possibility of disguising isolated locations of high concentration by mixing with samples of lower concentration;

- not a problem with <u>small-scale</u> composites (~ 'cluster samples' over $< 1m^2$) - <u>Are</u> suitable for undisturbed sam



c) possibility of loss of volatile compounds during the compositing processes;

- also applies to spot/grab samples - needs separate treatment

d) difficulty of achieving an adequately mixed and representative sample;

- no sample is entirely representative (has uncertainty) but composite samples are <u>more representative if properly prepared</u> e) difficulty in undertaking statistical analysis of composited data.
- OK is uncertainty known (lower for composite sample if sampling target properly defined (e.g. small area, or one trial pit)
- 4.2 Setting investigation objectives- need to make sure measurements ~ FFP need Uncertainty values
- Approach also applicable to on site and *in situ* measurements (8.4 On-site testing)
 - make ref to EA (2009)* gives worked example

* ENVIRONMENT AGENCY (2009) Framework for the use of rapid measurement techniques (RMT) in the risk management of land contamination ISBN 978-1-84432-982-3



Conclusions

- 1. Clearer definitions of sampling, measurement uncertainty, sampling uncertainty (section 3)
- 2. Broader introduction to the importance of estimation and reporting of uncertainty, rather than assumption of 'representative' sampling (Sections 7.8 & 10.3)
- 3. 'Strongly recommend estimation of U from sampling' (Sections: 5.7.2 Decision 4)
- 4. Revised wording in Annex D to explain broader applicability and usefulness of duplicate method, e.g. for judging fitness-for-purpose
 - cite Eurachem Guide, rather than CLAIRE TB7, in Annex D
- 5. Recommend taking composite samples (over small area = *cluster sample*) if sampling uncertainty needs to be reduced (Sections 7.6.2.6 & 8.3.2)
- 6. State U approach also applicable to on site and *in situ* measurements making reference to EA (2009) (8.4.1 On-site testing)



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 - for application to on site measurements

