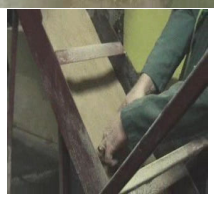
The way forward on Uncertainty from Sampling



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Sampling Uncertainty

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Overview

- Intended role of the UfS Guide
- Broader application to different media/situations (e.g. one-off batches)
- Balance between validation and QC
- Database of UfS/UoM (U of Measurement) estimates in different sectors – use as prior values?
- Uncertainty estimation using SPTs – better?
- Future research on UfS and UoM
- Conclusions on way forward

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Intended role of the UfS Guide

- Guidance for people who design sampling strategies
  - on how to incorporate estimation of UfS
- Make regulators aware of existence of UfS
  - and that there are methods available to estimate it
  - e.g. EU in Framework Directives, Codex for food
- Make analysts aware that
  - UfS exists and that
  - UoM estimates should include UfS
  - UfS is often greater than UfAnalysis
  - Sets FFP requirements for UfA in context

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Broader application of UfS Guide to different media/situations

- Guide only includes worked examples for one or two types of foods, feeds, water, soil
- Need to consider applications (e.g. how to take duplicates realistically) for
  - A wider range of situations for these 4 media (e.g. food at every stage from farm to fork)
  - Many other media e.g. gases, particulates, sediments, pharmaceuticals, metals etc..
  - Non-repetitive situations and one-off samples (e.g. forensic, local authority trading standards)

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Balance between validation and QC

- Many method in the Guide are practical and feasible at the validation stage of a method, but
- QC procedures need further development to check whether the conditions present at validation are still present and whether estimates of U are still applicable.
  - Especially an issues with sampling, where subsequent targets may be very different (e.g. contaminated land)
- Integrated approach to QC in the form of SAQC (Sampling and Analytical Quality Control)
  - Identify when out-of-control measurements are being caused by the analytical method, not by the sampling

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Database of UfS/UoM estimates - as prior values ?

- Useful to start compiling database of UfS/UoM estimates for each different sector
- Might be useful as prior values, e.g. for
  - Quality Control charts
  - For 'default values' when there is not enough resources, or time, to run a full validation
  - Help regulators decide on realistic expectations (limit?) for UfS
    - *Some evidence for useful prior values in contaminated land*

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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.

Assess the alternative methods, such as #4 using SPTs

1 estimate analytical bias using CRM, 2 Analytical bias partially or completely included where multiple labs involved

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Uncertainty estimation using SPTs

Toosey & Ramsey (2008)

- Principle explained in the UfS Guide
- Enables incorporation of contribution to UoM from any potential sampling bias (not included by the duplicate method)
- Few published examples for soil [1,2] and gas[3]
- New application of SPT to on-site measurements – pH in open water bodies:-

1. Ramsey, M.H. and Argyraki A.(1997) Estimation of measurement uncertainty from field sampling: implications for the classification of contaminated land. Science of the Total Environment, 198, 243 – 257
2. Squire, S., Ramsey, M.H., Gardner, M.J. and Lister, D. (2000) Sampling proficiency test for the estimation of uncertainty in the spatial delineation of contamination. Analyst, 125, Issue 11, 2026-2031
3. Squire, S and Ramsey, M.H. (2001) Inter-organisational sampling trials for the uncertainty estimation of landfill gas measurements. Journal of Environmental Monitoring, 3, 3, 288 - 294

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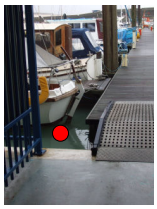
U estimation for on-site measurement using SPT approach



- Target: Water
  - Round 1 = pond (fresh water),
  - Round 2 = marina (sea water)
- Analyte: pH
  - measured on-site with portable meter
- Participants: same 8 for both rounds
  - Each given broad written objectives
  - calibrate and sample/measure independently/sequentially
  - Take 2 samples, 2 analyses on both samples
    - ≈ Duplicate Method on one target
  - Organiser interpolated a replicate procedure in Round 2
    - To see the effect of one sampler, sampling 8 times
  - Reference sampling target (RST) provided at one site
    - pH = 8.0 *(5l of 0.1 M sodium benzoate)* ≈ Matched to pH of this sea water

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Results of Water SPTs

- ANOVA separates

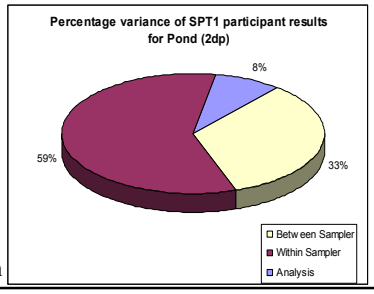
$$s^2_{total} = s^2_{between-sampler} + s^2_{within-sampler} + s^2_{analytical}$$

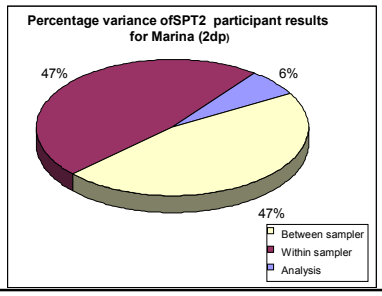
- u from 'duplicate method' from

$$s^2_{duplicate\_method} = s^2_{within-sampler} + s^2_{analytical}$$

- U from SPT method from s^2_{total}

Large between sampler contribution





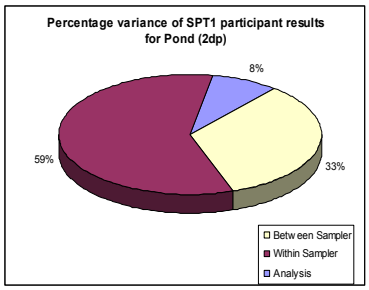
Sources of U in Water SPTs

SPT1 on Pond shows:-

•Main source in 'within-sampler' sampling variance

•Analytical contribution small

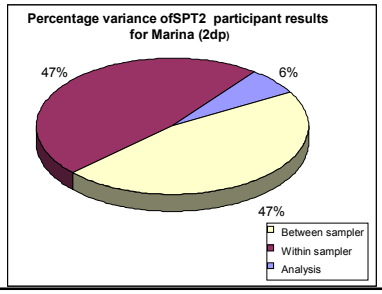
•Large contribution from between-sampler effects (e.g. sampling bias)



SPT2 on Marina:-

•Similar findings

•Greater contribution from between-sampler effects



Results of Water SPTs

	Robust estimates	**Duplicate Method**		**SPT method**		
Target	Mean pH	U	U%	U	U%	
Pond	6.60	0.54	8.18	0.66	10.0	
Marina - participants	7.98	0.17	2.13	0.24	2.99	
Marina - organiser	*7.97*	*0.10*	*1.25*	*0.12*	*1.54*	**Bias**
RST- participants	7.70	0.05	0.63	0.20	2.58	-0.30
RST - organiser	*7.97*	*0.11*	*1.35*	*0.11*	*1.35*	-0.03

- SPT approach gives higher (20-40%) estimate of U – more realistic
  - Except for organiser on RST (SPT = Duplicate Method)
  - Single sampler (organiser) with 'SPT' gets much lower U ≈ duplicate method
- U higher for pond – more heterogeneous? less buffered? 1st/2nd round?
- RST allows to estimation of overall bias – extra component of U
- z-scoring shows one participant has Z > 2 on SPT 1(pond)
  - with external FFP standard deviation requirement of 0.2 pH units
  - More development of scoring system for SPTs required

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Future research on UfS and UoM

- Estimation of UfS (as part of UoM)
  - Application to on-site and *in situ* measurements
  - Assessment of the SPT approach (real and virtual)
  - Comparison between different approaches
    - some big differences found already
    - e.g. x6 (136% modelling/23% empirical) on pistachio nuts[1]
  - Cost-effective estimation of UfS
  - UonU - we never know the true value of uncertainty
    - How many duplicates? Are 8 enough[2]?
    - Can UonU be estimated for modelling approach?

1. Lyn, J.A., et al.., Analyst, 2007, 132, 1231 - 1237
2. Lyn, J.A., et al. Analyst, 2007, 132, 1147-1152

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Future research on UfS and UoM(2)

- Expressing U if U% gets >50% or even > 100%
- Acceptable levels of UfS = FFP – improve & test criteria
- Interpretation of UfS information
  - E.g. for compliance, or risk assessment
- Modifying UfS, in order to achieve FFP
  - Why some systems behave in predictable ways ($s^2 \propto 1/m$)
    - and others don't
- Considering measurement process as a whole
  - e.g. MPTs rather than SPTs+APTs

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Conclusions on way forward

1. Get estimating and reporting UfS (within UoM) accepted as a requirement in good science & in regulation/compliance
2. Clarify ways to administer and manage the whole measurement process
   - i.e. Identify who is responsible for the quality (i.e. U) of sampling, sample prep and analysis
3. Encourage improved quality of sampling (more explicitly appropriate to the FFP requirement)
   - Better education, training and assessment of sampler *e.g. existing EU Leonardo Project*
   - Encourage funding bodies to support further research in UfS *– e.g. on items listed above*
4. Decide on how to regulate UfS
   - Set limits on UfS , e.g. UfS ⭘ 20% ??. or…
   - Encourage case-specific FFP criteria?
   - Include rational decisions of sampling frequency/spacing using Cost v. UfS
5. Encourage users of measurements to use and propagate the UoM (inc UfS) values in their interpretation (e.g. in HHRA, epidemiology, and compliance)

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