Uncertainty of Measurement from sampling, preparation and chemical analysis

Michael H Ramsey FRSC
School of Life Sciences,
University of Sussex, Brighton, UK
m.h.ramsey@sussex.ac.uk

Uncertainty in Contaminated Land Risk Assessment. RSC-Tox SOBRA. Burlington House London, 17 December 2009

University of Sussex

Overview

- Uncertainty (U) in general (e.g. in Risk Assessment)
- Uncertainty of Measurements (UoM)
  - Measurement process – includes sampling & prep
- Methods for estimating uncertainty of measurements
  - e.g. Guidance from *Eurachem/Eurolab/Citac/Nordtest/RSC-AMC*
- Benefits of knowing uncertainty
- Conclusions

Uncertainty in general

- Several types of uncertainty ranging from determinism and total ignorance (adapted from Walker *et al*., 2003)

- Separate concepts of **variability** (spread of true values), from **uncertainty** (U) (Kelly & Cambell, 2000)
- U - includes all contributions to the estimated (rather than the true) distribution of values, that come from imperfect knowledge.
- **Uncertainty** can be reduced , e.g.:-
  - U of measurement - by taking larger sample mass
  - U-of-mean value - by repeated measurements
  - but **variability** cannot be reduced.
- Statistical uncertainty – is the most quantitative form, one example is...
- Uncertainty of measurement

Walker, W.E., Harremoës, P., Rotmans, J., van der Sluijs, J.P., van Asselt, M.B.A., Janssen, P. and von Krauss, M.P.K. 2003 Defining uncertainty. A conceptual basis for uncertainty management in model-based decision support. *Integrated Assessment* 4, 5-17
Kelly, E); Campbell, K. (2000) Separating variability and uncertainty in environmental risk assessment - Making choices. Human and Ecological Risk Assessment, 6 (1): 1-13

University of Sussex

Uncertainty of measurement (inc. sampling)

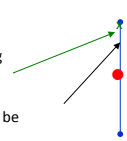
- U of measurement is:-
  - *Informally:*- the interval around the result of the measurement that contains the **true value** with high probability
  - *Formally:-*
    - *An estimate attached to a test result which characterises the range of values within which the true value is asserted to lie (ISO, 1993*)*
    - *Non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used (VIM, 2008**)*
  - 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 all steps in measurement (e.g. sampling & prep)
- Key parameter of measurement (and sampling) quality
  - Encompasses effects of other parameters of analytical methods,
    - e.g. bias, precision, detection limit, etc.
- Doesn't assume measurements (or sampling) are 'correct'

**ISO 3534-1: 1993 Statistics – Vocabulary and Symbols, International Organization for Standardization, Geneva*
***International Vocabulary of Metrology – Basic and General Concepts and Associated Terms. VIM, 3rd edition, JCGM 200:2008*

University of Sussex

Uncertainty of Measurement (UoM)

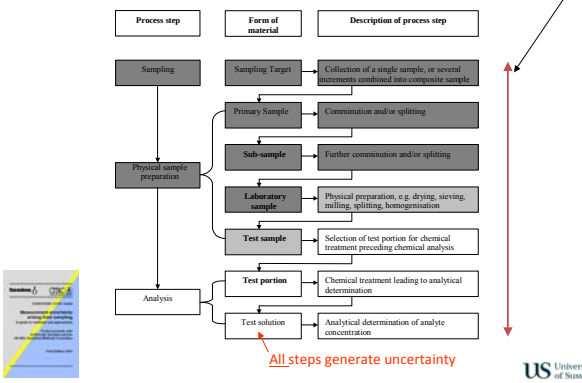
- *The interval around the result of a measurement that contains the true value with high probability*
  - *e.g. U =20% on measurement of 390 mg/kg Pb*
  - *Range of U = 390+20% =468 mg/kg*
    to 390-20% =312 mg/kg
- We can never know the true value *(could be 460 mg/kg)*
- Effect on comparison with threshold value of 450 mg/kg
  i.e. Measured value 390 mg/kg is below the threshold value
  True value 460 mg/kg is above the threshold value
  Measured value gives 'false negative' classification
- All we need to know is how far from the truth we might be
  - *e.g. with 19/20 chance if being right = 95% confidence*
- Different from U on mean value (used in CIEH/CLAIRE Guidance)
- How can we estimate uncertainty of measurements
  - including that from sampling?
  - Eurachem Guide* has methods for estimating measurement uncertainty
  - including that arising from sampling
  - *Has applications to soil, groundwater, food, gas*



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

University of Sussex

Measurement Process – Starts with sampling



University of Sussex

Four empirical methods for UoM

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.

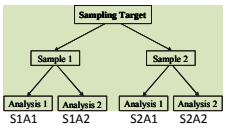
Simplest Empirical method is 'Duplicate Method' (#1)

1 Estimate analytical bias using CRM (Certified Reference Materials),
2 Analytical bias partially or completely included where multiple labs involved

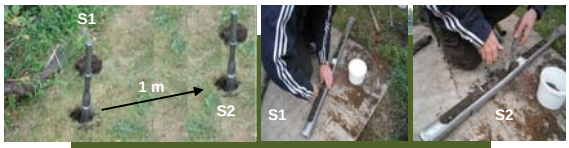
US University of Sussex

The Duplicate Method

- Define your sampling target and sampling protocol (Exploratory or Main)
- Use a balanced design



- Take a sample at the nominal sampling target.
- At 10% of locations (n≥8) - take a second sample displaced from the original (in space or time) to reflect the ambiguity in the sampling protocol
- Carry out duplicate analyses on both the sample duplicates
- Estimate uncertainty components using Robust ANOVA



US University of Sussex

Case Study #1: Duplicate Method

for estimation of UoM in hazard assessment

The scenario:

- 9 hectare on former landfill, in West London
- Potential housing development
- key contaminant → Pb
- Need to delineate area areas >SGV
- Prior to site-specific risk assessment
- 100 sampling locations – in regular sampling grid, 10 x 10, spacing 30 m →
- top soil samples (0 – 0.15 m) - collected using a sampling auger
- survey conducted with measuring tape and compass
  - U in relocation ~ 3m (- similar to that using typical GPS)

Eurachem UfS Guide: Example A2

US University of Sussex

Study design – Duplicate Method

- Duplicate samples taken at 10 sampling locations (i.e. 10%) randomly selected.
- 3 m from the original in a random direction
- 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

US University of Sussex

Sample prep and analysis in the lab

- 6 soil CRMs were selected for analysis to assess the analytical bias over a range of concentrations
- Measurements subject to full AQC – but not assumed to be 'true' values of concentration
- Corrected for reagent blank concentrations where statistically different to zero
- Raw measurements for estimation of uncertainty were:
  - untruncated – e.g. 0.0124 mg/kg not < 0.1 or < detection limit
  - unrounded – e.g. 2.64862 mg/kg not 3 mg/kg

US University of Sussex

Results – map of Pb contamination

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

Argyraki (1997)

Only 16/100 locations over UK SGV = 450 mg Pb/kg

— mainly 'uncontaminated' = below action limit (84%)

- US_{95} (235 mg Pb/kg) < 450 mg Pb/kg – no action

- The max value at location B2 (3590 mg Pb/kg) was shown to be a population outlier

US University of Sussex

Results from Duplicate Method

- 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
E8	229	215	208	218
F7	346	374	525	520
			77	73
H5	56	61	116	120
I9	189	189	176	168
J5	61	61	91	119

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

Components of UoM
Random & Systematic

	s = u mg kg^{-1}	U =ks mg kg^{-1}	U_{meas}' = 200. s_{meas} / $\bar{X}$	% of U_{meas}
Analysis	11.1	22.2	7.5%	0.8%
Sampling	123.8	247.6	83.3%	99.2%
Measurement*	124.3	248.6	83.6%	100%

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

- averaged over the 10 targets
- to represent the 100 targets
- Expressed in relative terms (%) for widest applicability

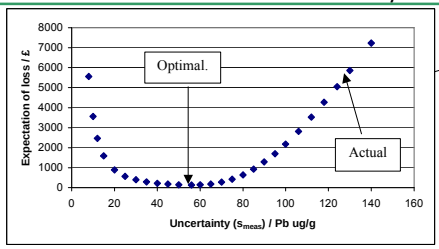
- **Systematic error – from Analytical Bias** estimated as 3.41 % ± 1.34 %
- By analysis of 6 CRMs – bias modelled as function of concentration
- $U_{systematic}' = 2.\sqrt{(3.41^2 + 1.34^2)} = 7.33$ %
- Adding in this uncertainty
- $U_{total}' = \sqrt{(U_{random}^2 + U_{systematic}^2)} = \sqrt{(83.63^2 + 7.33^2)} = 83.95$
- Effectively identical to estimate based on just random components
- Does exclude bias from primary sampling – other methods required

If site mean is the measurand?

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

    = 200 $\frac{se}{\bar{X}}$ = 200 x $\frac{40.3}{291.9}$ = 27.6 % of the mean value

Optimal Uncertainty vs Actual
for West London Case Study

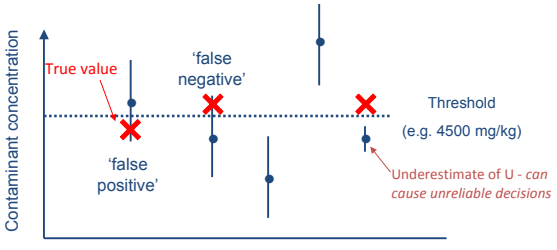


- False Positive at c = 700µg g^{-1} unnecessary remediation

- Loss predicted at actual uncertainty £5680 per location
- £130 at optimised uncertainty - save 96%
- 3 fold reduction in U_{samp} indicated (e.g. by taking 9-fold composite samples)
- Judge Fitness-for-purpose of measurements – (not use labs criteria e.g. 10%)

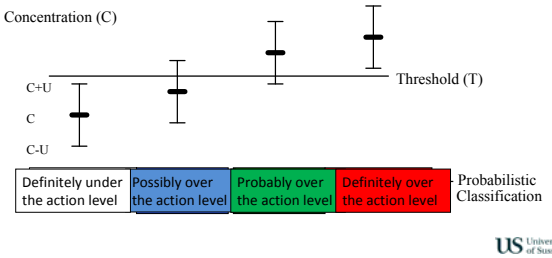
Ramsey et al.,(2002) J. Env. Monitoring, 4, 5, 809 - 814

Benefits of Knowing UoM
→ make more reliable decisions



Probabilistic classification

- 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:



Probabilistic classification- Mapping

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

41% of locations at least 'possibly over the action limit'

US University of Sussex

Case Study 2. Metal working site

- Former industrial landfill site in the UK.
- approx. 1.68Ha area
- Used for waste disposal for approximately 40 years.
- Exact nature of the wastes deposited at the site are unknown
- Suspected to contain elevated concentrations of heavy metal and organic (potentially diesel, hydraulic,rolling and heavy fuel oils and lubricating greases) contaminants.
- Experiment designed for comparison of on-site versus lab-base measurement uncertainty

Boon K.A., Ramsey M.H. McKenna S., and Yeo M. (2008) The use of measurement uncertainty to assess the reliability of on-site field test kits for the investigation of contaminated land. Proceedings of ConSoil 2008 (10th International UFZ-Deltares/TNO Conference on Soil-Water Systems), Milan, Italy, 3-6 June 2008 (ISBN: 978-3-00-024598-5). Theme C, 64-73

US University of Sussex

Case Study 2 - Methods
- field sampling and preparation

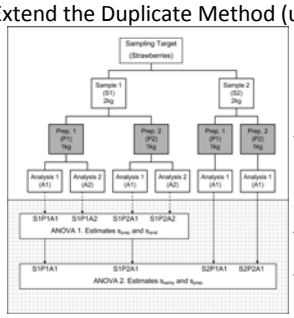
- 11 trial pits in stratified random sampling design
  - Excavated using mechanical digger

- Primary sample (4-fold composite) collected from pile of soil at side of pit for each 0.5 m interval.
- Total of 62 samples were collected.
- Duplicate Method (+CRMs) used to estimate U:-
  - Duplicate samples at 8 sampling locations
  - by reinterpreting the sampling protocol.
- Primary sample prepared in the field
- Measurements both in field (and in lab), for TPH (Total Petrol Hydrocarbons) and others (PAH, metals)
- Extra duplicates to estimate UoM from sample preparation
  - Design from Eurachem Guide

US University of Sussex

UoM from Sample Preparation

- Extend the Duplicate Method (unbalanced design)



Extra layer of duplication to estimate uncertainty from sample prep

2 rounds of ANOVA to separate U_{prep} from $U_{sampling}$ & $U_{analysis}$

Eurachem UfS Guide (2009) Appendix D, and
Lyn, J.A., Ramsey, M.H., Fussel, R.J. and Wood, R. (2003) Measurement uncertainty from physical sample preparation: estimation including systematic error *Analyst*, 2003, 128 (11), 1391 – 1398

US University of Sussex

Sample Prep Contribution to UoM
on Field measurement of TPH

	s (mg/kg)	U(%)	% of UoM
Sampling	173.0	32	49
Prep	125.4	32	26
Analysis	124.0	23	25

Combined 'U from Sampling' = 75%

- *Using modified Duplicate Method – with extra sample prep duplicates*
- *Robust ANOVA to separate & quantify variance*
- *Show that U from 'Sampling' (as usually defined) contributes 75% of UoM*
- *~35% of this arises from Sample Preparation = substantial - in this case*
- *Lab measurements of TPH also high U (U_{anal}% = 32%)*
  - *even though accredited method (lab's estimate of U_{anal} much lower ~ 15%)*
  - *Lab sample prep also hidden source of uncertainty – not reported*

US University of Sussex

Conclusions (1)

- Uncertainty arises at every step in risk assessment,
  - but Uncertainty of Measurement (UoM) is often overlooked
- UoM can affect both the construction of RA models
- - and its interpretation = double effect
- UoM is not negligible just because measurements are made in a 'accredited' lab
  - as analytical uncertainty can be unexpectedly high in reality
  - Most uncertainty arise from the sampling and sample preparation (UfS not quoted by the lab)
  - dominates the budget of measurement uncertainty
- Methods are now available to estimate UoM (inc UfS) (Eurachem Guide)
  - applicable to many media such as soil, water, air, wastes, food, feed *etc.*
  - New *Support Tool for Reliable Environmental Measurement (STREM)* includes methodologies

US University of Sussex

Conclusions (2)

- New methods now revealing the size of the UoM for the first time
  - examples in Cont Land often 50 - >150%
  - extra information that adds to *U of mean value* used in CIEH/CLAIRE Guidance
- Knowing UoM enables:-
  - Propagation of UoM into Human Health Risk Assessment
    - random component can be overwhelmed by other sources (e.g. dose-response),
    - but systematic component remains
    - hence more reliable RA and environmental management decisions
    - example for Blood Lead published*
  - Ability to compare different sources of UoM, see which is limiting
    - decide whether to reduce that sources
      - e.g. take samples with larger mass or more increments
    - Don't rely on labs estimate of $U_{analytical}$
  - Enable the concept of 'optimal' levels of UoM = Fitness-for-purpose of measurements
    - decided by risk assessor – not the lab
    - can enable substantial cost-savings on site development overall
    - minimum UoM not always required – not cost effective
  - Enables better use of on-site measurement tools
    - higher U_{anal}, but cheaper so take more samples – lower overall U.

Ramsey, M. H. (2009). Uncertainty in the assessment of hazard, exposure and risk. Environmental Geochemistry and Health, 31, 2, 205-217, doi:10.1007/s10653-008-9211-8

US University of Sussex

Acknowledgements

Co-workers:
- Steve Ellison (Co-author on Eurachem Guide)
- Dr Katy Boon (TPH study in Case Study #2) ,
- Dr Ariadne Argyraki (Case Study #1),
- Dr Paul Taylor (Fitness-for-purpose),
- Dr Jenny Lyn (Sample Prep U)

Funding:
- EPSRC (Studentship)
- NERC (NE/E009484/1 Environment and Human Health call)
- UK Department of Trade and Industry (now TSB, Partners in Innovation STBF/004/00034C)
- UK Technology Strategy Board (TSB) Technology Programme (Project Number - TP/5/CON/6/I/H0065B).
- CL:AIRE (RP4)
- UK Food Standards Agency (E01034, E01055, E01070)

US University of Sussex