Sampling, ***and the uncertainty it causes in measurements***

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Overview

- Sampling as part of the measurement process
- Methods for estimating uncertainty of measurements 'U' (inc. sampling) – with examples
  - Eurachem/Eurolab/Citac/Nordtest Guide
- Benefits of knowing uncertainty
- How much uncertainty is acceptable?
  - To ensure reliable compliance decisions
- Conclusions

Sampling as part of the measurement process

- Sampling traditionally considered separately from measurement.
  - Design ‘correct’ sampling protocol to give a representative sample
  - Train sampler to apply the protocol,
    - then assume that is applied ‘correctly’ – no quality control
- Sampling really the first step in the measurement process
  - *In situ* measurement techniques reveal this
  - Place the sensor→ make measurement = taking a sample
  - Uncertainty in sampling produces U in measurement
  - Depends on the objective of the measurement

Sampling as part of the measurement process

- If the objective is to measure the true value
  - of the analyte concentration (or measurand)
  - in the sampling target *(e.g. batch of food)*
- Sampling is included in measurement process
- U from sampling part of measurement uncertainty*

- If true value (or measurand) defined solely in terms of laboratory sample
  - sampling is not included

* Ramsey MH (2004) Accred Qual Assur., 9, 11-12, 727 - 728

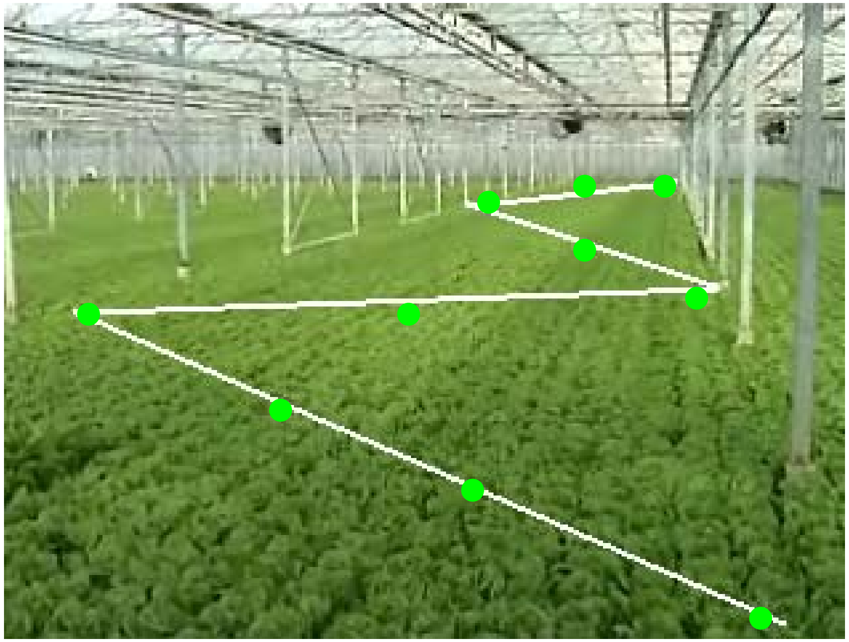
Methods for estimating uncertainty of measurement *(including sampling)*

- What are the options?
  - 'Top down' methods
    - based on replicate measurements (within or between organisations)
    - applicable to any system
  - 'Bottom up' methods
    - based on identifying, estimating and summing all of the components
      - (Kurfurst *et al*, 2004, Accred Qual Assur., 9, 64-75)
    - sometimes uses Gy's Sampling Theory to estimate components
      - (Minkkinen 2004, Practical applications of sampling theory, Chemometrics and Intelligent Lab. Systems, 74, 85-94)
    - applicable to some particulate systems
  - Covered in Eurachem/Eurolab/Citac/Nordtest Guide
- Simplest is the top down 'Duplicate Method'
  - *explain with case study*

Case Study 1
Nitrate Concentration in Lettuce

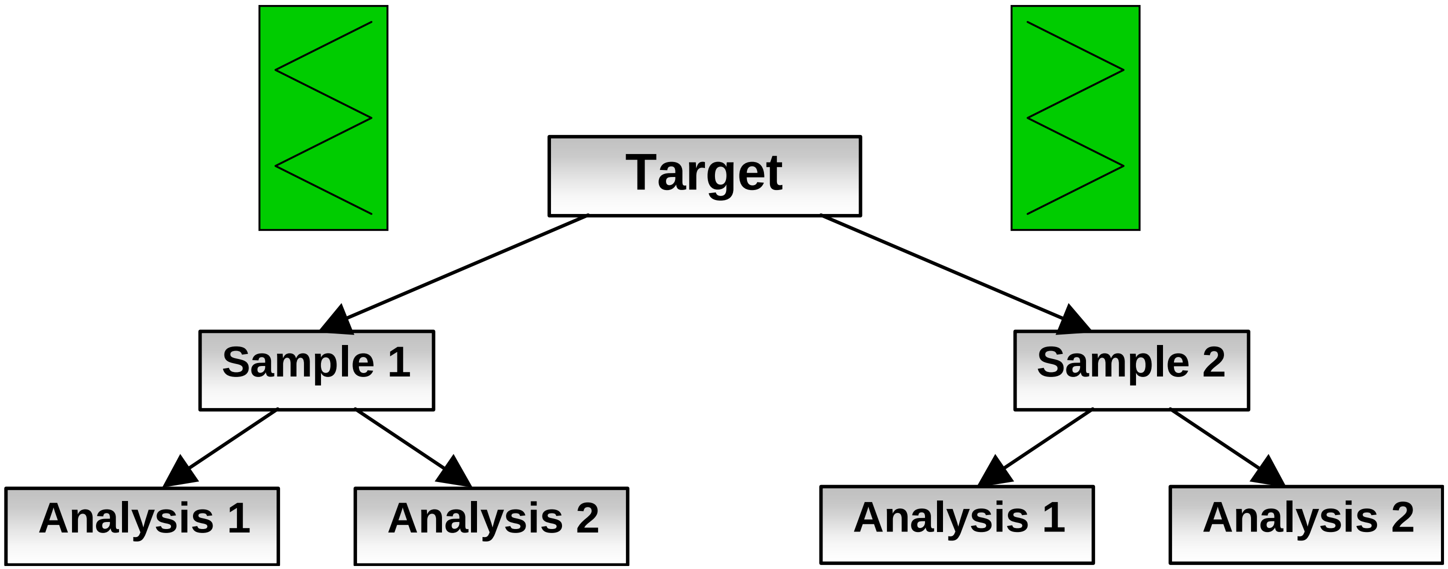
- Nitrate a potential risk to human health
- EU threshold 4500 mg/kg for batch concentration
- Current sampling protocol specifies taking 10 heads to make a single composite sample from each batch *(in ‘W’ or ‘star’ design)*
- Usual ambiguity in the protocol
  - *e.g. where to start and orientation*
- What is the uncertainty in measurements?

‘W’ Sampling Design for Lettuce

Duplicate is equally likely interpretation of ‘W’ design

Estimating U with **Duplicate Method** using **Balanced Design**



At 10% of Sampling locations in whole survey $n \geq 8$

Nitrate conc. in Duplicate Samples

mg/kg

S1A1	S1A2	S2A1	S2A2	
3898	4139	4466	4693	
3910	3993	4201	4126	
5708	5903	4061	3782	
5028	4754	5450	5416	>4500?
4640	4401	4248	4191	
5182	5023	4662	4839	
3028	3224	3023	2901	<4500?
3966	4283	4131	3788	

Most analytical duplicates agree well < x0.1 (approx)

Sampling duplicates agree only < x0.2 (approx)

Range of conc. between batches x1.6 (approx)

Is level of Uncertainty OK?

Reliable decisions whether batch is > 4500 mg/kg?

Uncertainty estimate for Lettuce

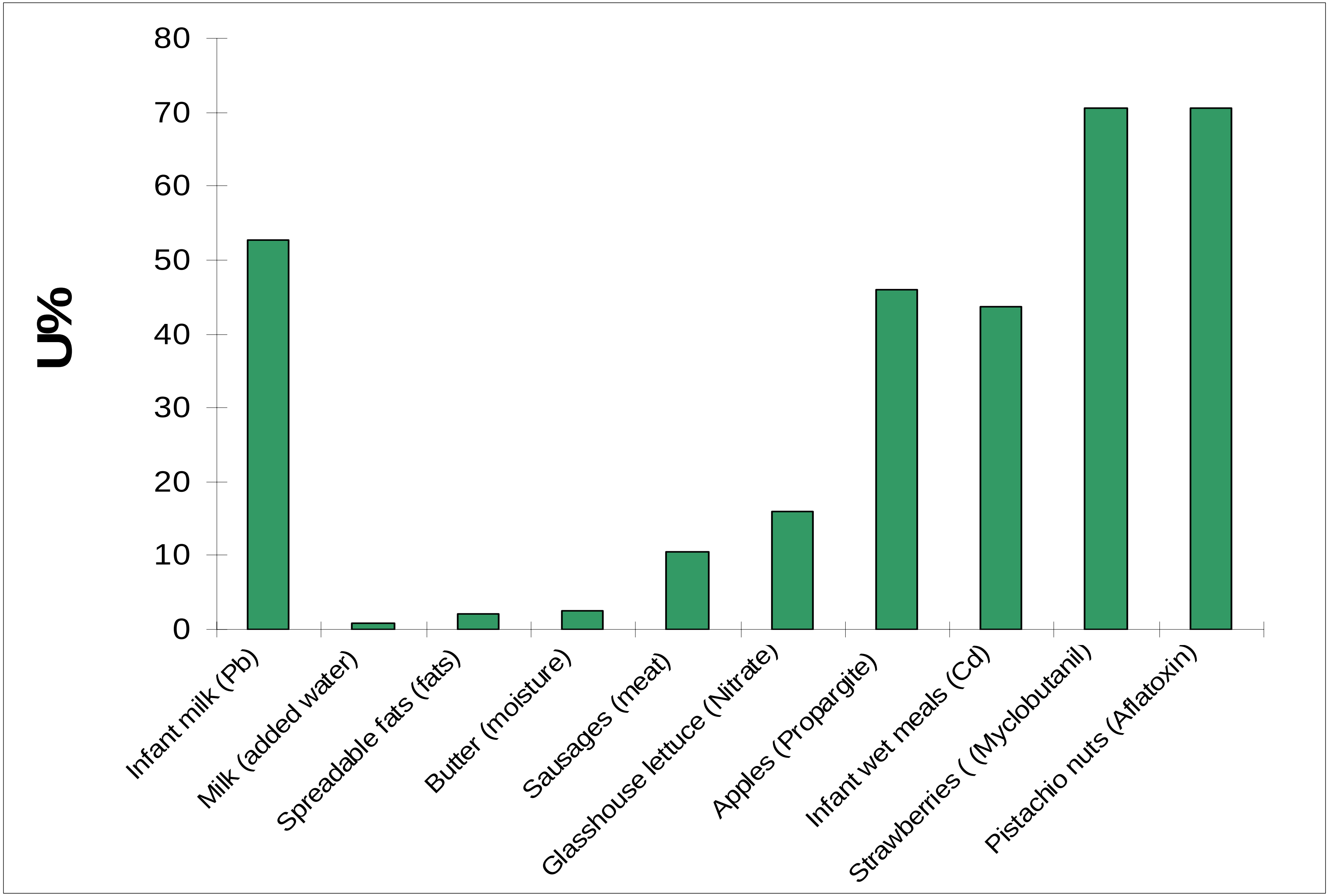
- Uncertainty = 361 mg/kg
- = 16% *relative to the concentration value (at 95% confidence)*
  - Calculated from measurements on duplicates
  - Using Analysis of Variance (ANOVA)
    - Robust statistics to accommodate outlying values
  - U from analytical bias (from CRM/ or spike)
    - can be added – not detected in this case
- Does not include U from any sampling bias
  - Can be included using values from Sampling Proficiency Test (SPT) – with >8 organisations

U estimates for other foods

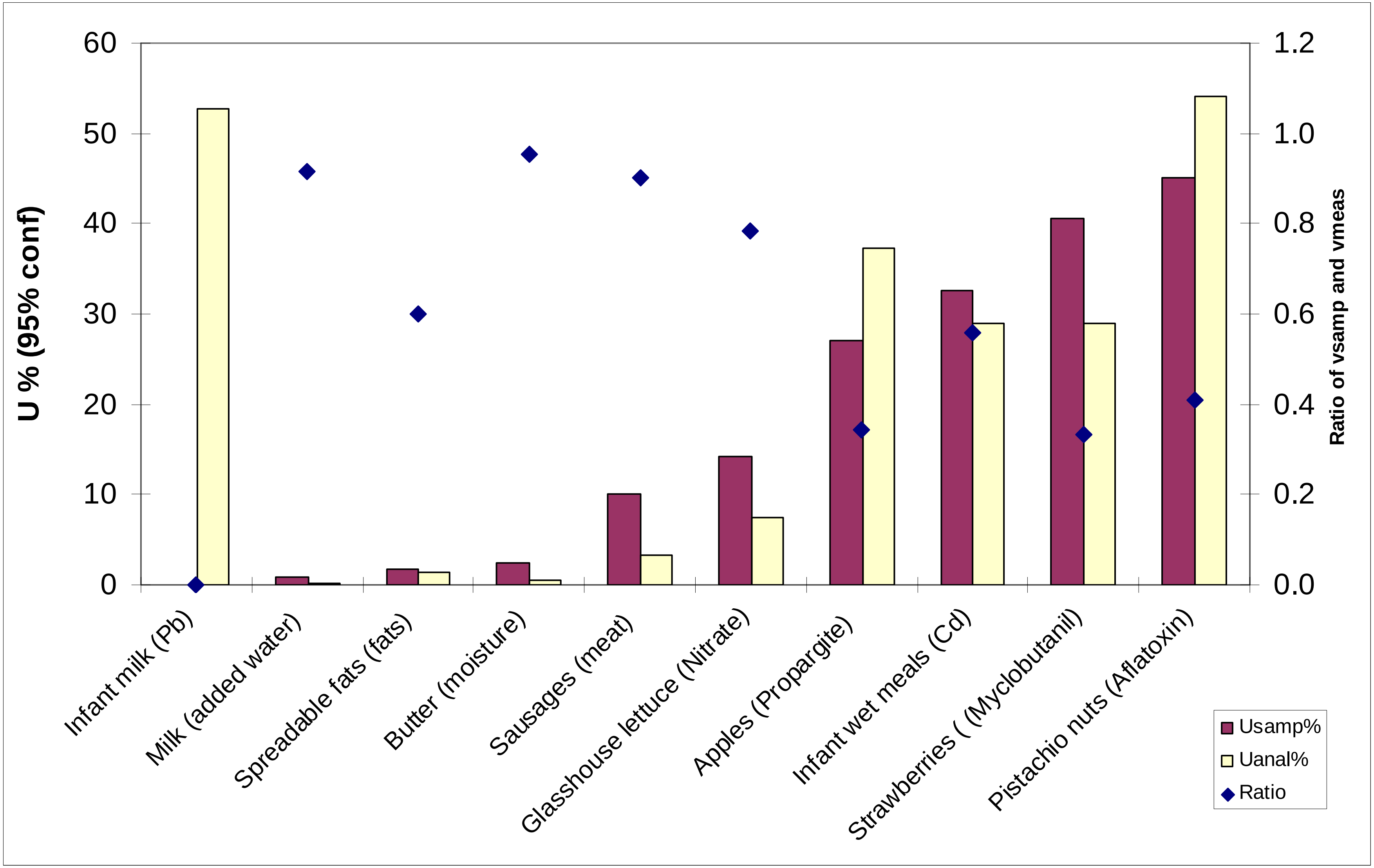
- Applied Duplicate Method to sampling 10 different foods/analytes, range of costs, heterogeneity, situations

Product	Analyte	Costs (£)			
		Sampling	Analysis	False non-comp	False comp
Infant milk	Pb	15.51	45	400,000	100,000
Milk	Added water	8.33	10	500	5 000
Spreadable fats	Fat	2.44	60	3000	5 000
Butter	Moisture	4.5	7.5	4590	18680
Sausages	Meat	14.35	90	100	2 000
Glasshouse lettuce	Nitrate	40	40	2400	2640
Apples	Propargite	195	83	5000	1000000
Infant wet meals	Cd	8.71	45	2,000	100,000
Strawberries	Myclobutanil	10	80	5000	100000
Pistachio nuts	Aflatoxin	6.29	60	5,000	50,000

U estimates for other foods



Components of U



Benefits of Knowing Uncertainty

- **Benefit #1:-**

Improving reliability of compliance decisions

  - *e.g. for Lettuce*

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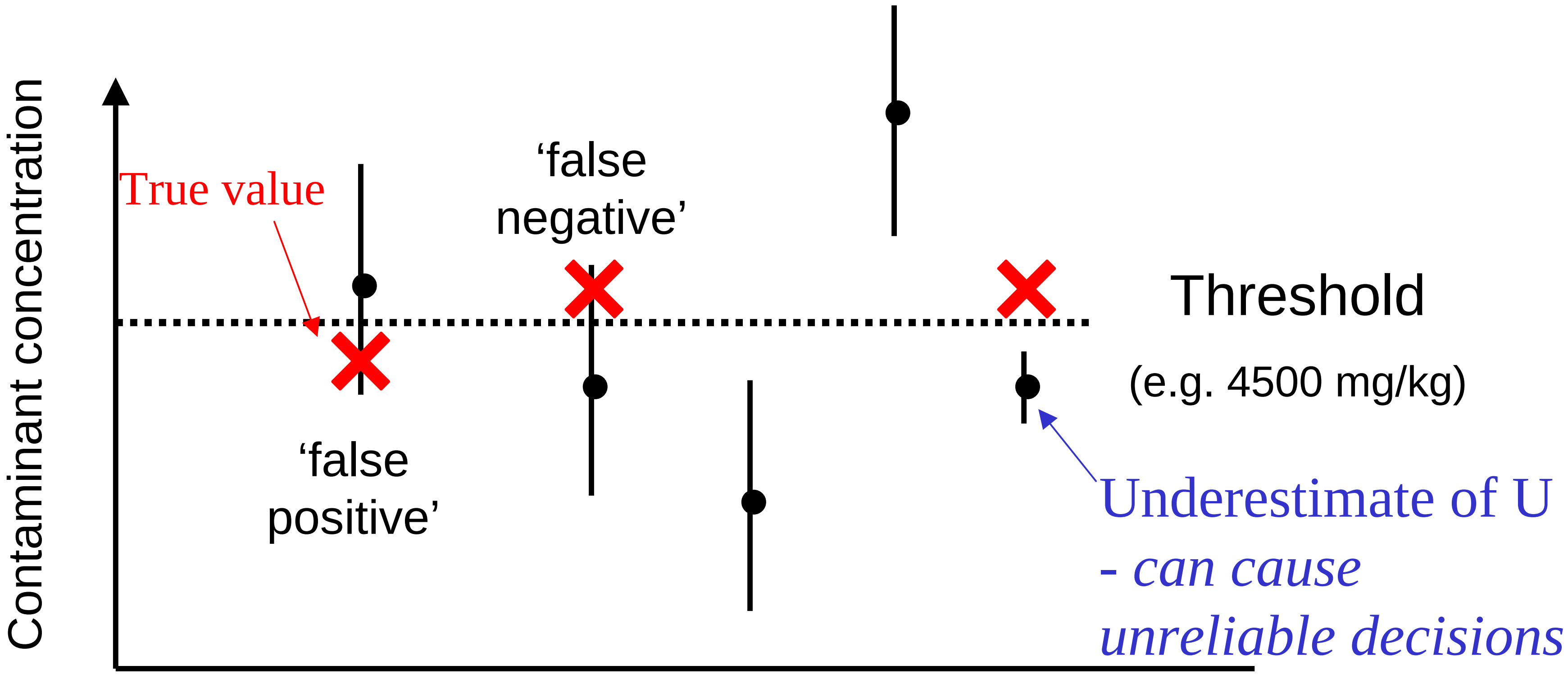
Know the U → make more reliable decisions



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Benefit #2 of Knowing Uncertainty

Judging fitness for purpose

- *e.g. for Lettuce* 

Acceptable level of Uncertainty?

- How can you judge if you have too much uncertainty?
- One option -use the optimised uncertainty (OU) method*
- Balance the cost of measurement
- against the cost of making incorrect decisions

* Lyn, J.A., **Ramsey, M.H.**, and Wood, R. (2002) Analyst, 127, 1252 - 1260

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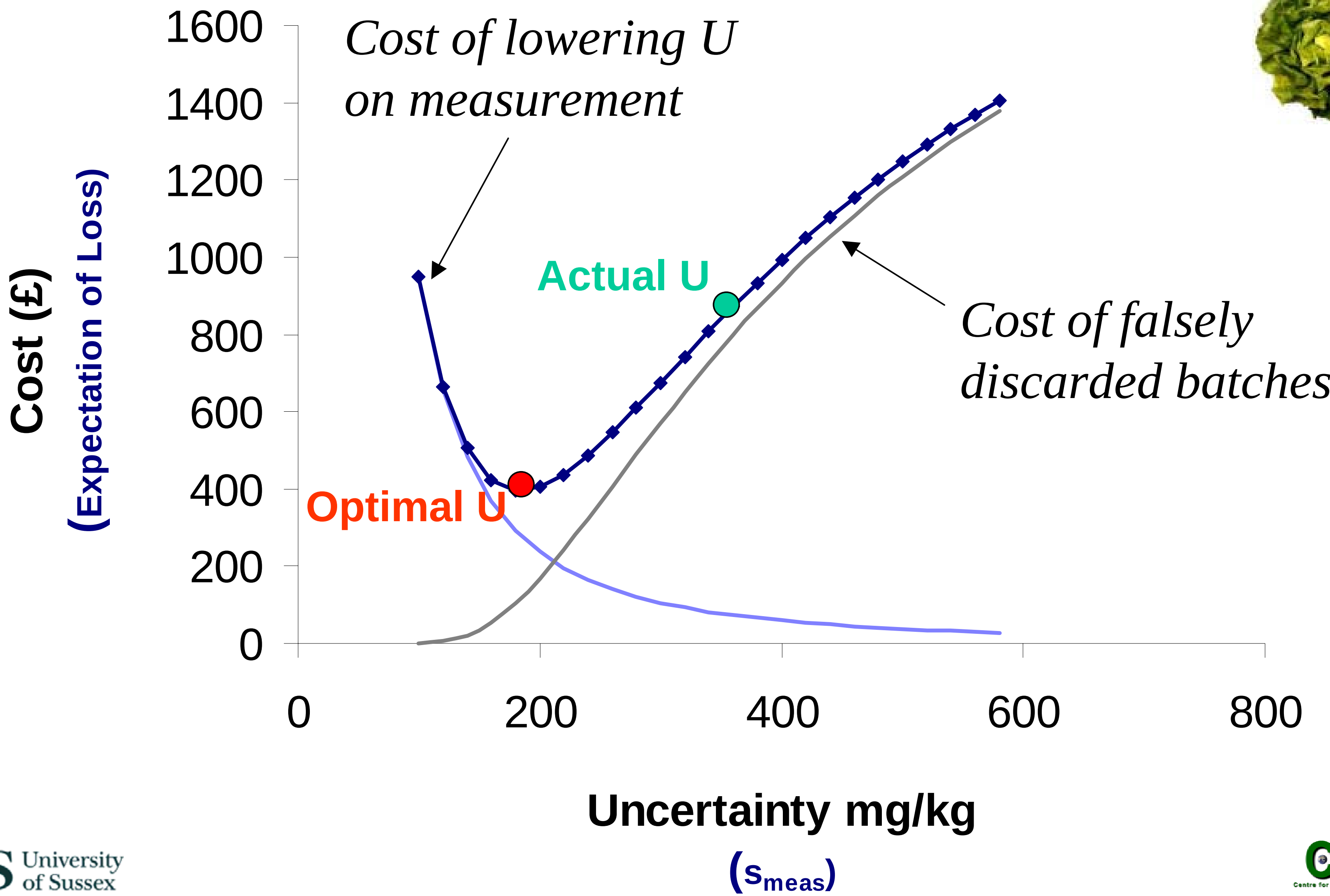
Acceptable level of Uncertainty?



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Benefit #3 of Knowing Uncertainty

Rational basis for allocation of finance,

to:-

1. Measurement as a whole, and
2. Apportionment between sampling and analysis

Allows achievement of optimal uncertainty

- and fitness for purpose of whole measurement method

– *e.g. Lettuce*

Achieving Optimal Uncertainty

- Graph shows that U is too high – need to reduce it
- Need to know source of U
  - from sampling or from chemical analysis?
  - balanced design + ANOVA - tells us sampling 78% of U
- We need to reduce the U by a factor of 2 (360→180)
- Gy's sampling theory predicts that we can do this by increasing the sample mass by factor of 4 (= 2^2)
- Reduction in U was achieved in practise → FFP
  - By taking composite sample with 40 heads instead of 10

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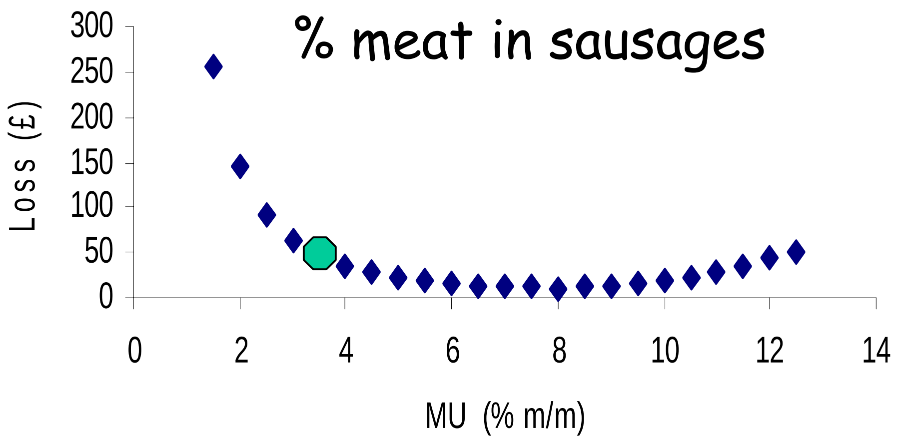
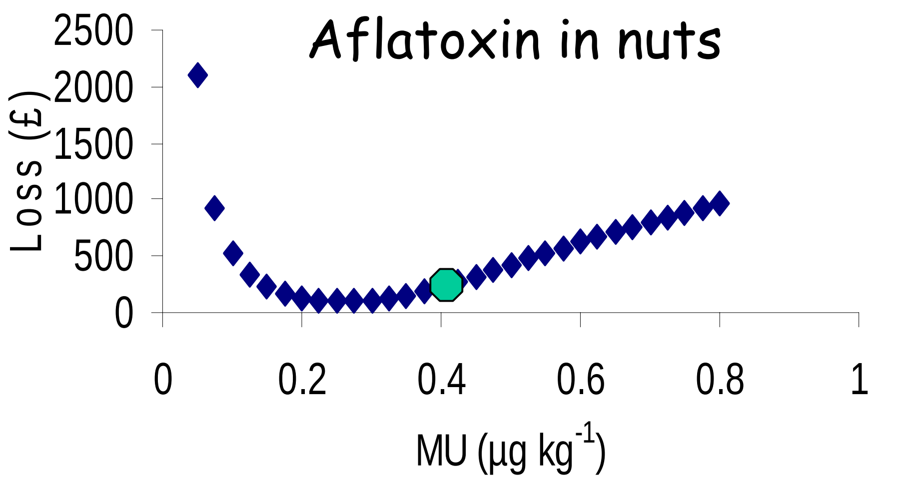
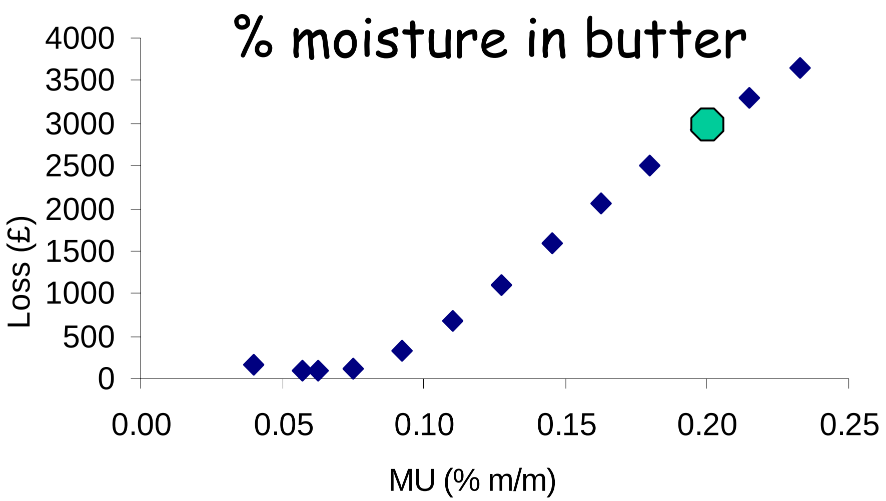
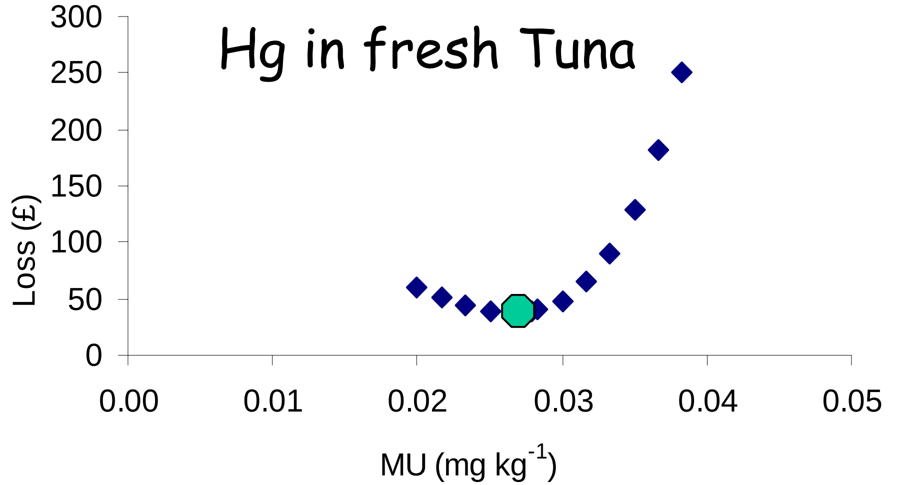
Optimising sampling of other foods









Benefits #4 of Knowing Uncertainty

Provides tool for monitoring Quality of Sampling

- Better than assuming ‘correct’ sampling
- Gives quantitative estimate of sampling quality
- Tool to improving quality
  - and training and accredit samplers
- Bring sampling within similar QC to analysis

Future work

- Most reliable estimate of uncertainty?
  - needs a method to judge reliability
  - Current work on Uncertainty on Uncertainty (UonU) (fig)
- Most cost-effective estimate?
  - Comparing the performance of different methods of U estimation
  - Compare UonU against cost
  - E.g. SPT results expensive, but does include sampling bias
- How often do uncertainty estimates need to be updated?
  - Not like estimates of analytical uncertainty
  - Sampling U affected by heterogeneity of batch
  - may vary from batch to batch – needs updating/checking with sampling QC

Conclusions (1)

- Sampling is best considered as part of the measurement process
- Methods are available to estimate the uncertainty of measurement
  - Generated by all of the steps (including sampling)
  - Some methods are going to be more feasible than others
  - Choice of methods will depend of the type of food (e.g. particulate? modelable?), UonU requirement, and cost of estimation.

Conclusions (2)

- Benefits of having full estimate of uncertainty:-
  - Improves reliability of compliance decisions
  - Enables judging fitness for purpose of measurements
  - Gives rational basis for allocation of finance
  - Provides tool for monitoring Quality of Sampling

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