# Uncertainty evaluation for analysis and sampling

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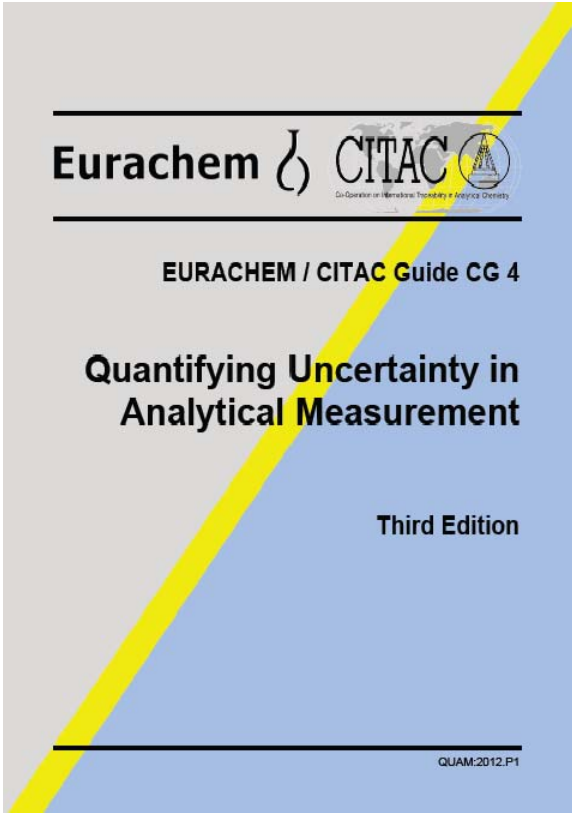
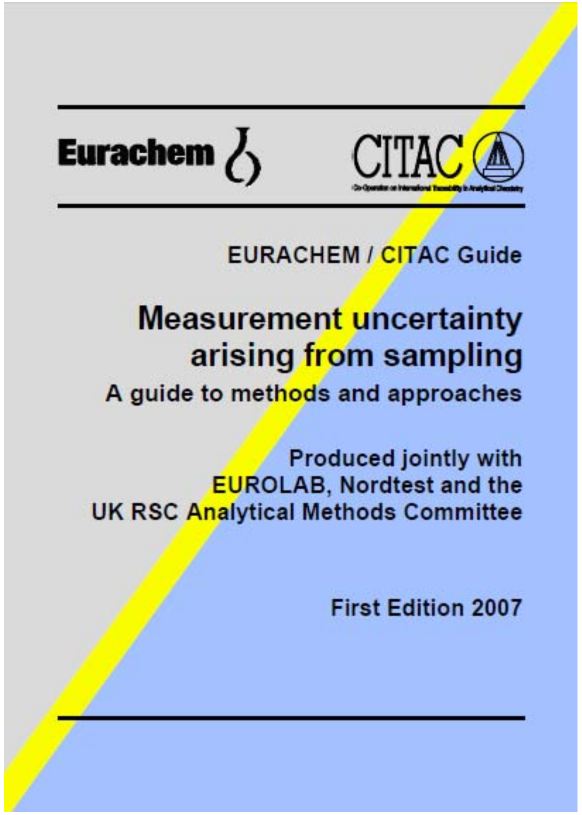
# Introduction

- Highlights from current guidance
- What's missing?



# Uncertainty evolution

**Pre-1978** Random/systematic error; Error propagation in chemistry (Eckschlager 1961); Collaborative study

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**1980**
- BIPM INC-1 (1980)
  - Type A / Type B
  - Combine as variances

**1982**
- AOAC Stats manual *(Development/validation)*

**1986**
- ISO 5725:1986 *(Collab trial)*

**1993**
- **ISO Guide**

**1995**
- EURACHEM Guide 1st ed
- ISO 5725:1994 *(Adds trueness)*

**2000**
- EURACHEM Guide 2nd ed (QUAM:2000

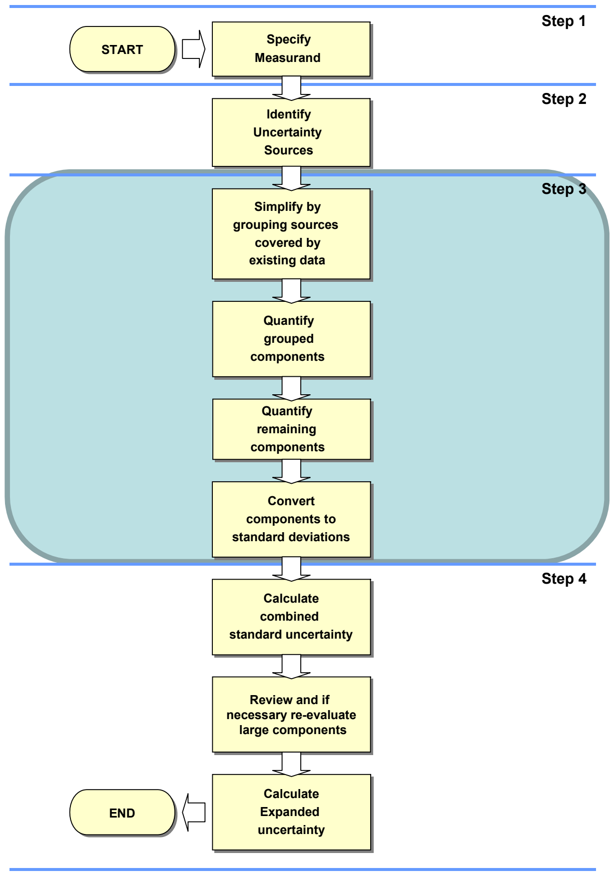
**2010**
- GUM Supplement 1 (MCS)
- *ISO 21748 – Uncertainty from collab study data*

**2012**
- **3rd Edition EURACHEM/CITAC guide published**

# QUAM:2012 Ch. 4. The Process of Measurement Uncertainty Estimation

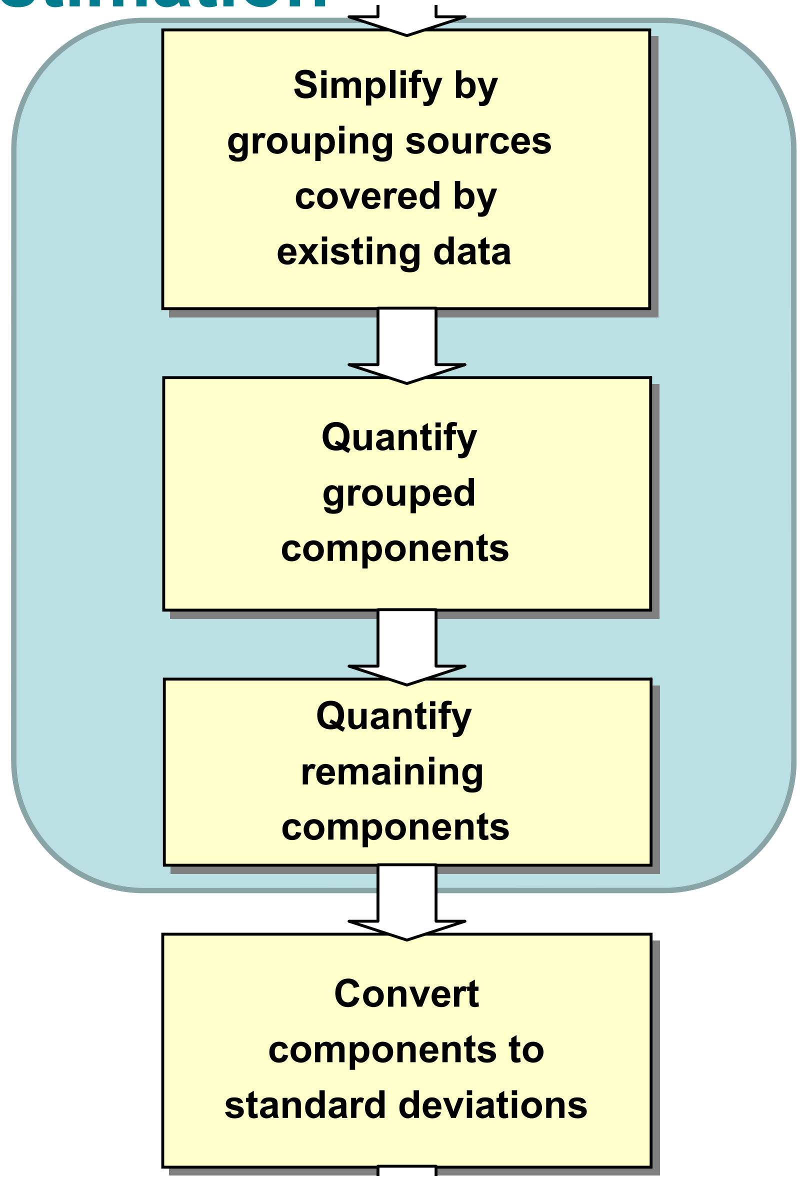
- Outline of the process
  - Specify measurand
  - Identify Sources
  - Group and quantify
  - Combine

- Unchanged in 2011

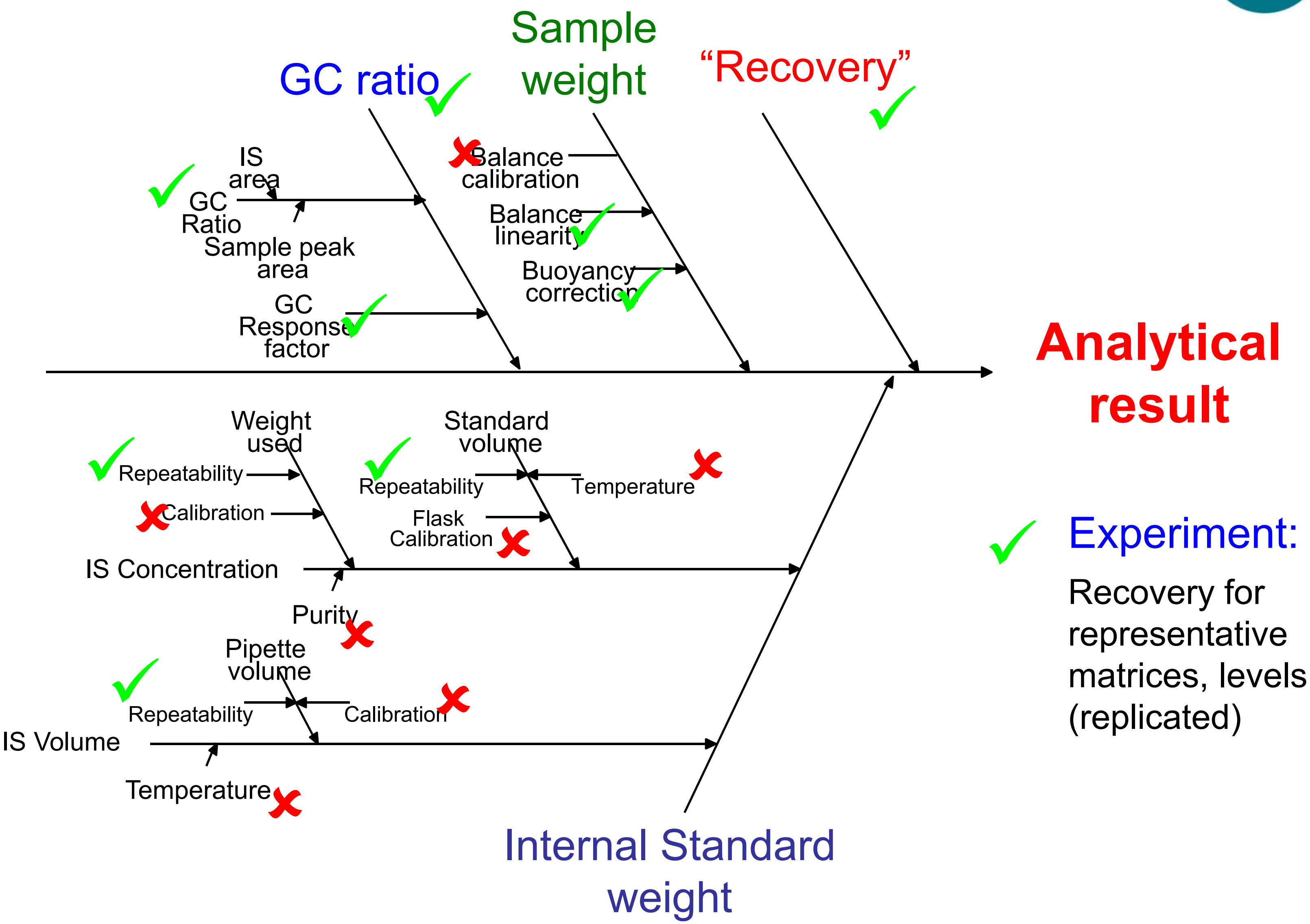


# Ch. 4. The Process of Measurement Uncertainty Estimation

Step 3



# Cause and effect analysis



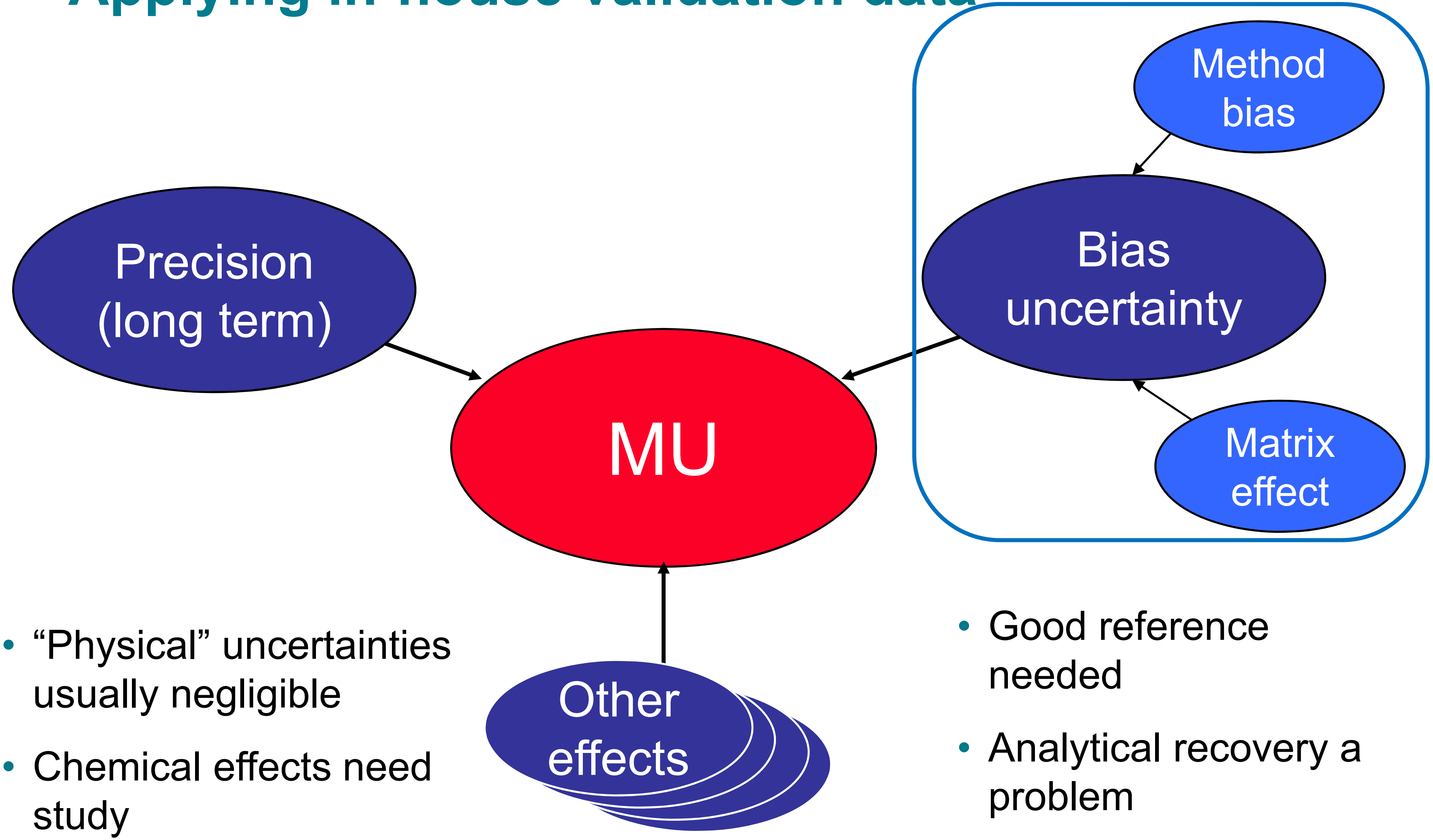

Experiment:

Recovery for representative matrices, levels (replicated)

# Ch 7: Quantifying Uncertainty

- Introduction and procedure
- Evaluating uncertainty by quantification of individual components
- Closely matched certified reference materials
- Uncertainty estimation using prior collaborative method development and validation study data
- Uncertainty estimation using in-house development and validation studies
- Data from proficiency testing
- Empirical and ad-hoc methods

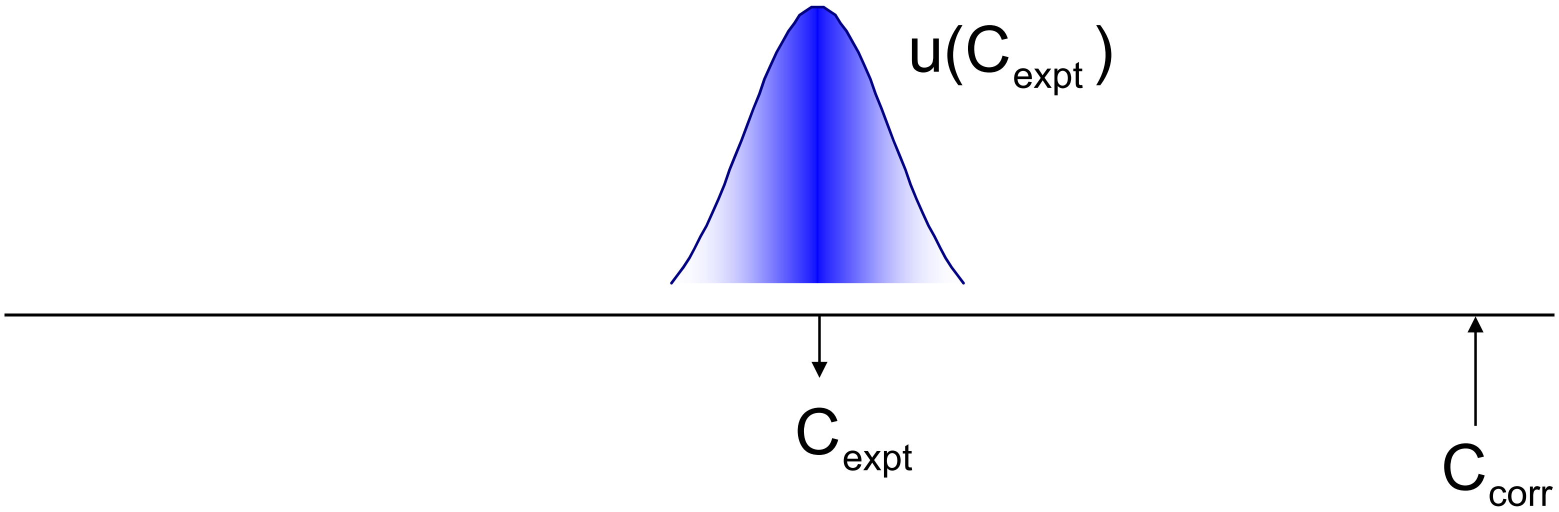
# Principle:
# Applying in-house validation data



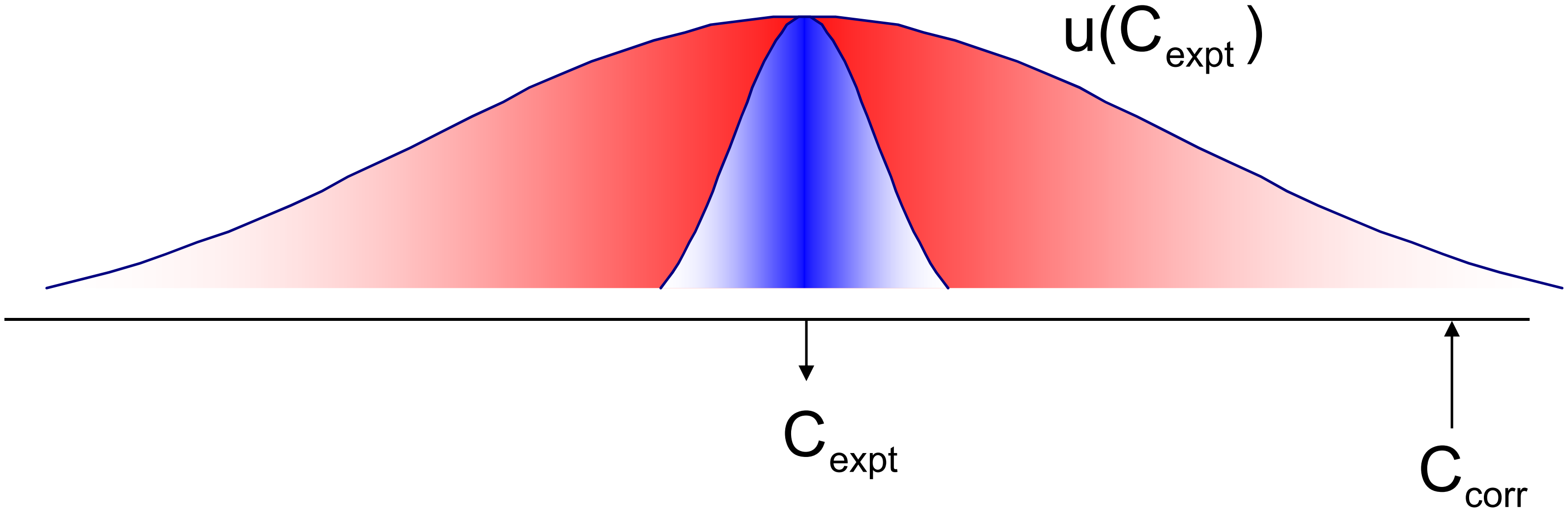

- "Physical" uncertainties usually negligible
- Chemical effects need study

- Good reference needed
- Analytical recovery a problem

# Significant bias without correction



# Significant bias without correction – increasing reported uncertainty




- Is this sensible?
- If not, what is the alternative?
- If so, how large an expansion?

# Different uncertainty expansion methods

$$U = k \cdot \sqrt{u(y_{obs})^2 + u_\Delta^2}$$

*(if bias significant)*

$$U_+ = k \cdot u(y_{obs}) - \Delta$$

$$U_- = k \cdot u(y_{obs}) + \Delta$$

$$U = k \cdot \sqrt{u(y_{obs})^2 + u_\Delta^2}$$

*(always included)*

$$U = k \cdot u(y_{obs}) + |\Delta|$$

$$U = k \cdot \sqrt{u(y_{obs})^2 + \Delta^2}$$

$$U = k \cdot \sqrt{u(y_{obs})^2 + \Delta^2 + u_\Delta^2}$$

$$U = k\sqrt{u(y_{obs})^2 + \left(\frac{\Delta}{k}\right)^2}$$

$$U = k\sqrt{u(y_{obs})^2 + \left(\frac{\Delta}{k}\right)^2 + u_\Delta^2}$$

... all of which are wrong at least some of the time.

# Sampling uncertainties

# QUAM:2012 - Identifying Uncertainty Sources

- A list of likely sources of uncertainty
  - Sampling
  - Storage Conditions
  - Instrument effects
  - Reagent purity
  - Assumed stoichiometry
  - Measurement conditions
  - Sample effects
  - Computational effects
  - Blank Correction
  - Operator effects
  - Random effects

# Does measurement uncertainty include sampling?

## EURACHEM position

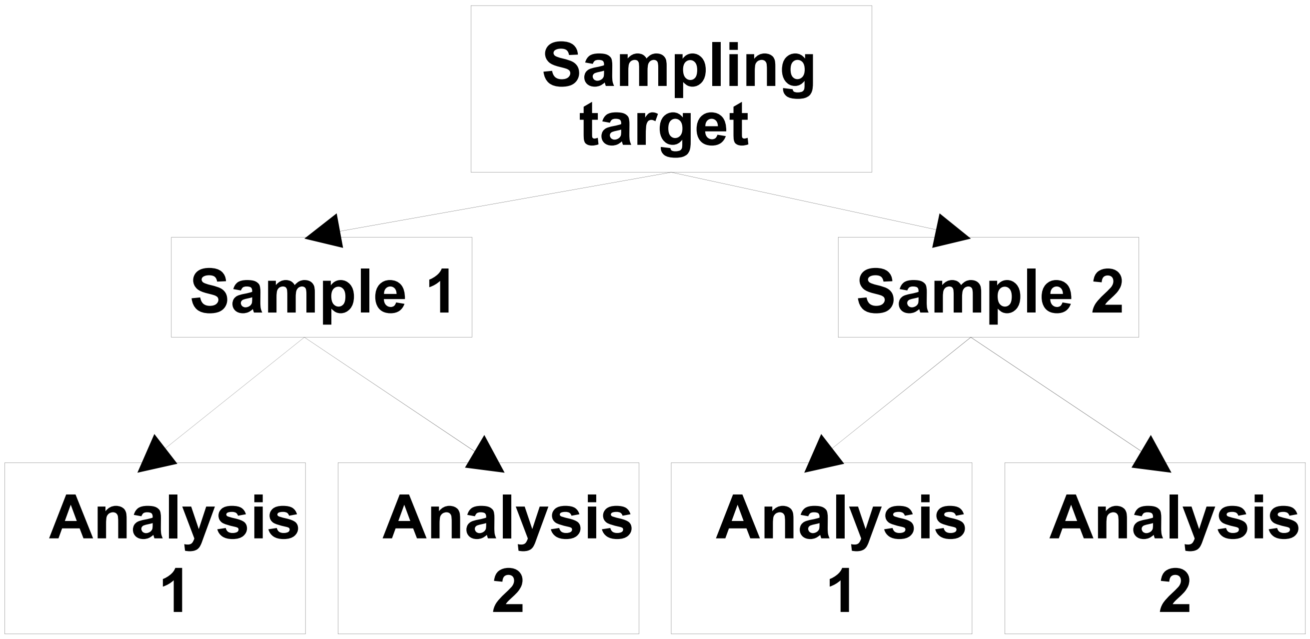
- If the measurand relates to a bulk material from which samples are taken for analysis, the uncertainty in the estimated value for the measurand must include the uncertainty arising from the sampling process

- If the result is reported on the sample ‘as received’ by the laboratory, only within-laboratory sub-sampling contributes to the uncertainty

# Different approaches to control of sampling

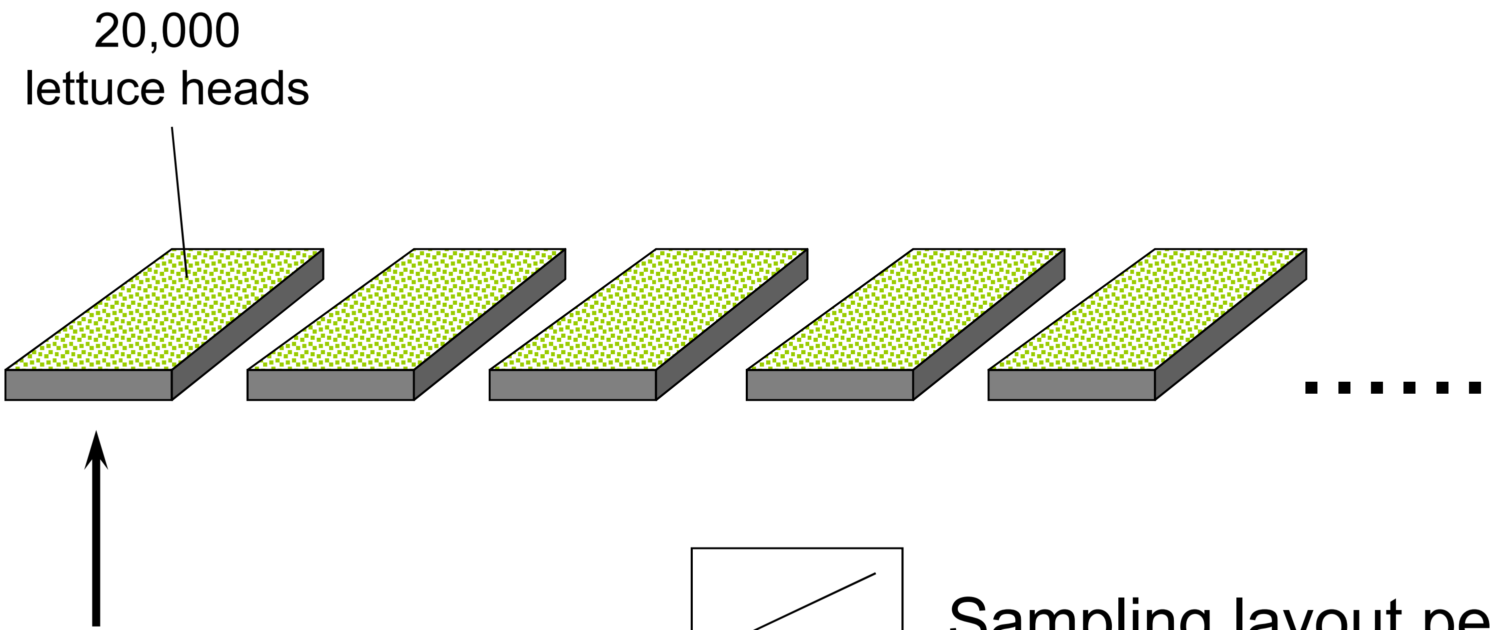
- Gy: Well respected, based on management and control to eliminate sampling uncertainties
- Sampling uncertainties quantified using replication
  - Ramsey et al
  - Eurachem Guide
- Applying modelling approaches to sampling uncertainty
  - Minkkinen et al

# Using the 'duplicate method'
# 1) Separating sampling and analysis

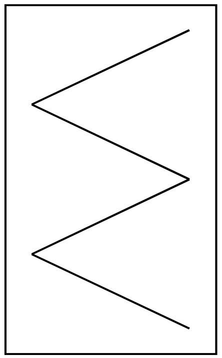



**Sampling target:**
Portion of material, at a particular time, that the sample is intended to represent.

# Example: Nitrate in lettuce (Eurachem Guide p 35ff)



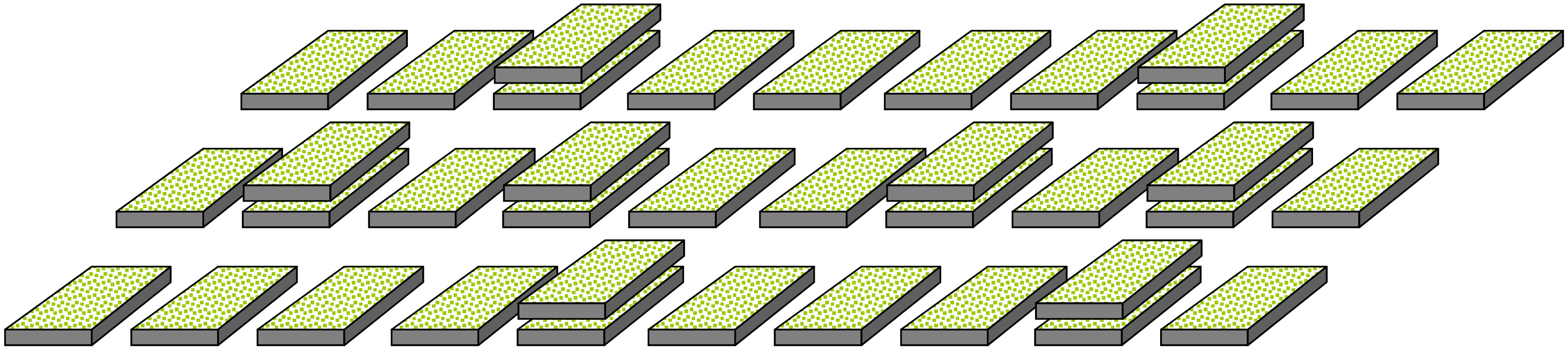

1 "sampling target"



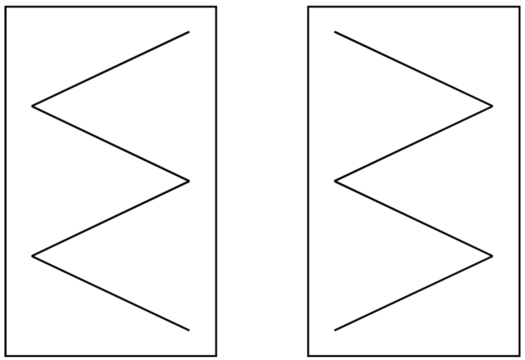
Sampling layout per bay:

- Every bay sampled
- Decision for each bay

# Duplicate method

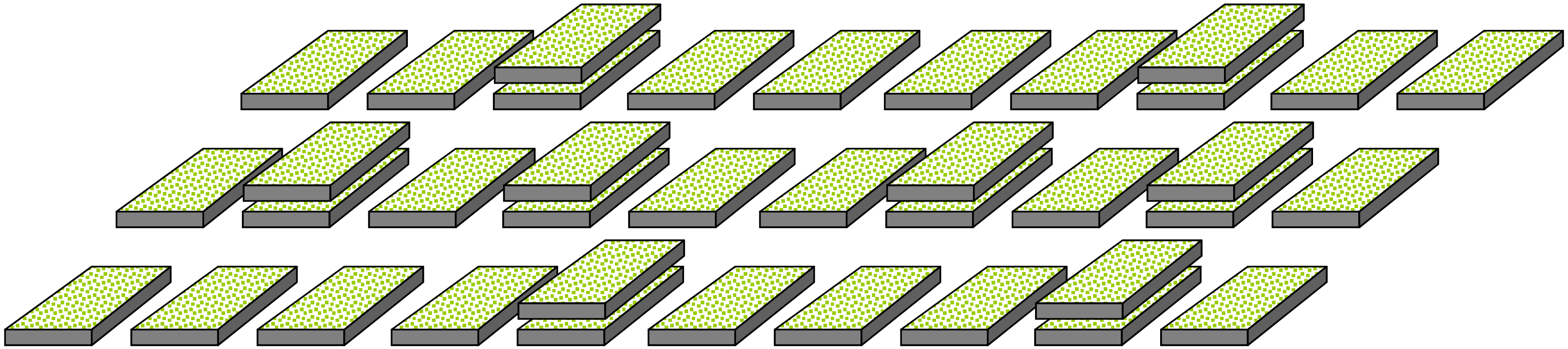


8 (or more) targets sampled in duplicate



Duplicate sampling arrangement

# Example: Analysis



Analysis 1

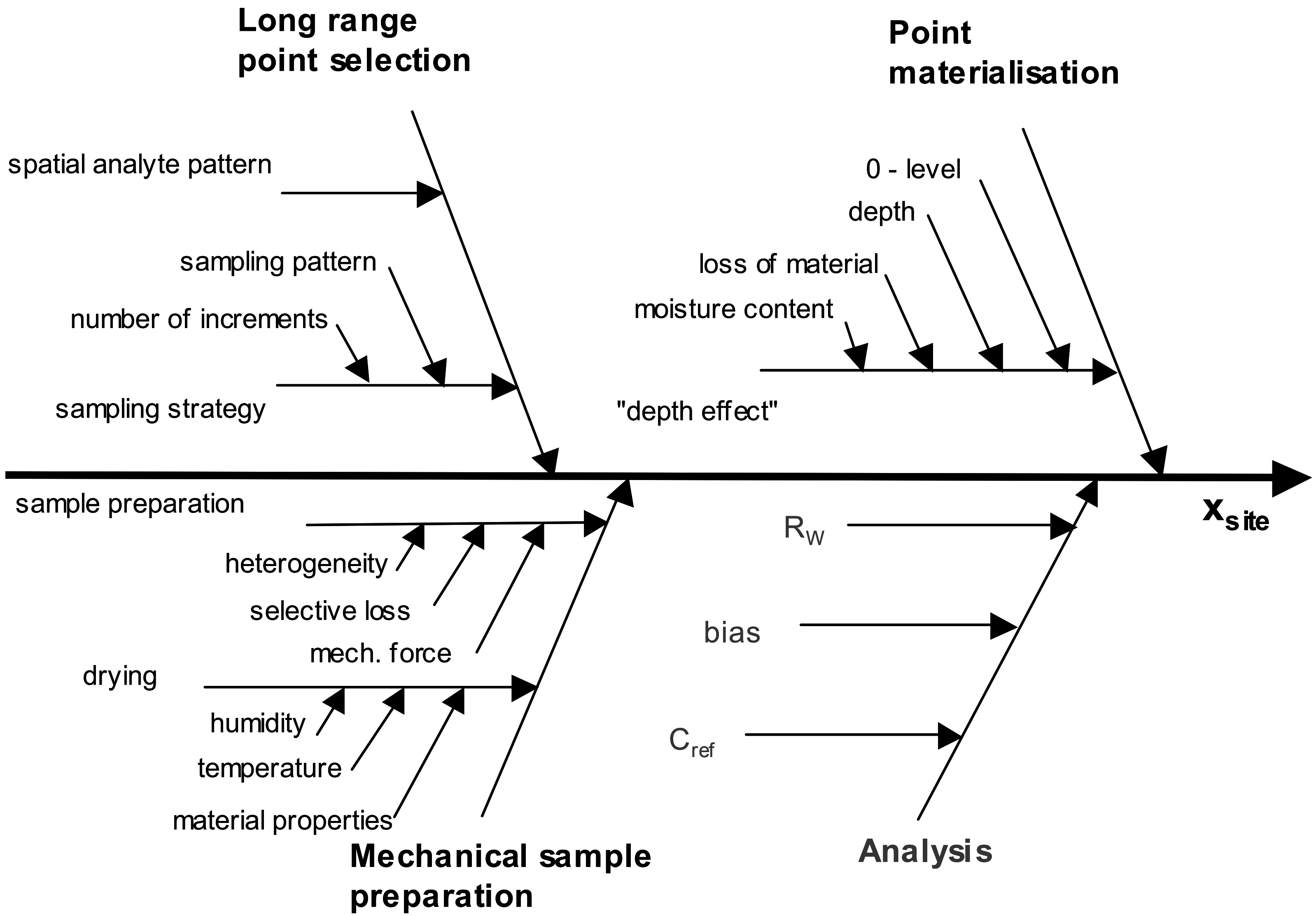
Analysis 2

8 sampling targets

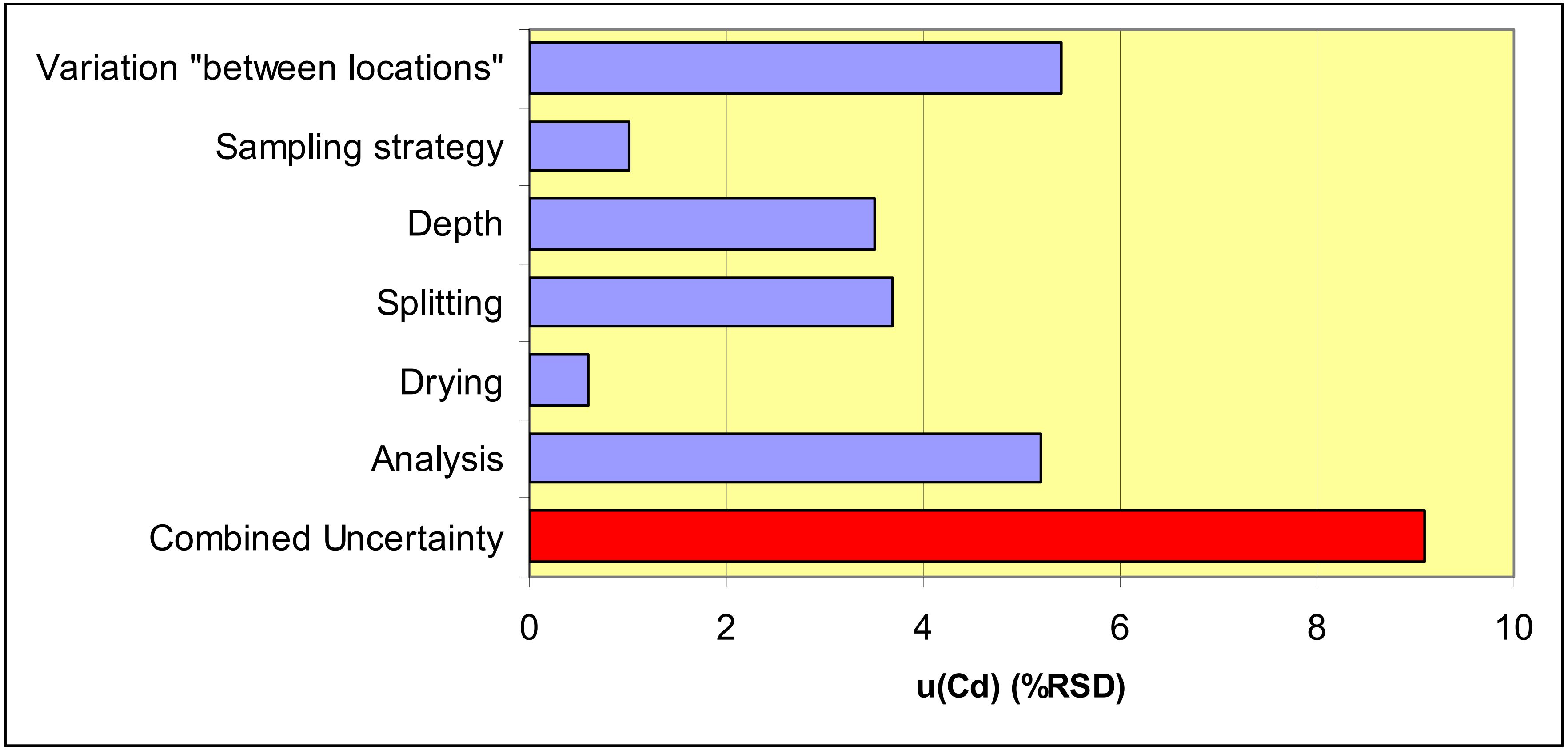
Sampled in duplicate

Each sample duplicate analysed in duplicate

# Modelling for sampling uncertainty: Cd and P in top soil



# Modelling for sampling uncertainty: Cd and P in top soil



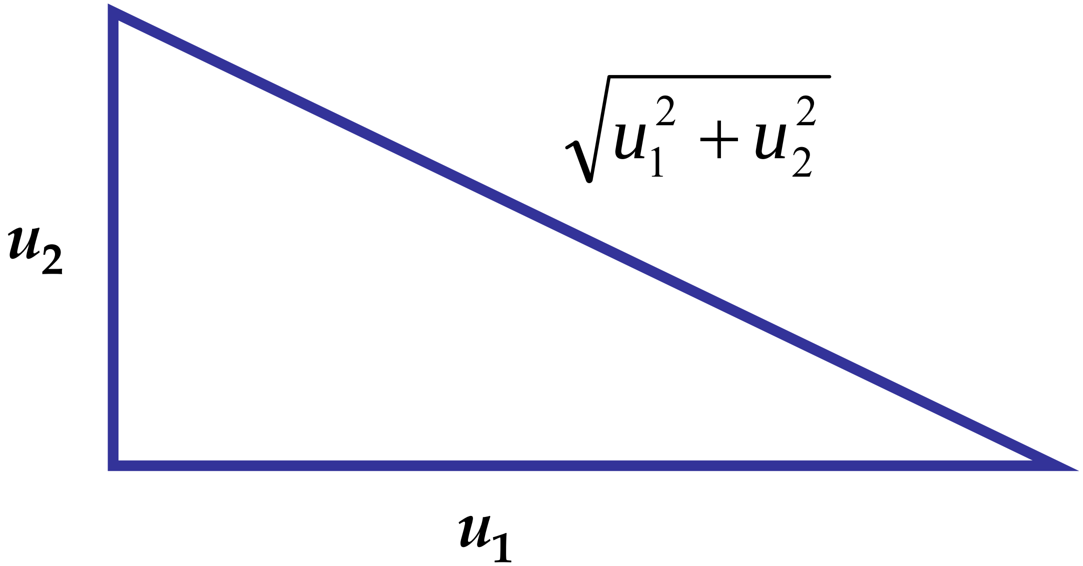

Note comments: “additional effort and cost is not appropriate for routine measurements.”

# A policy problem

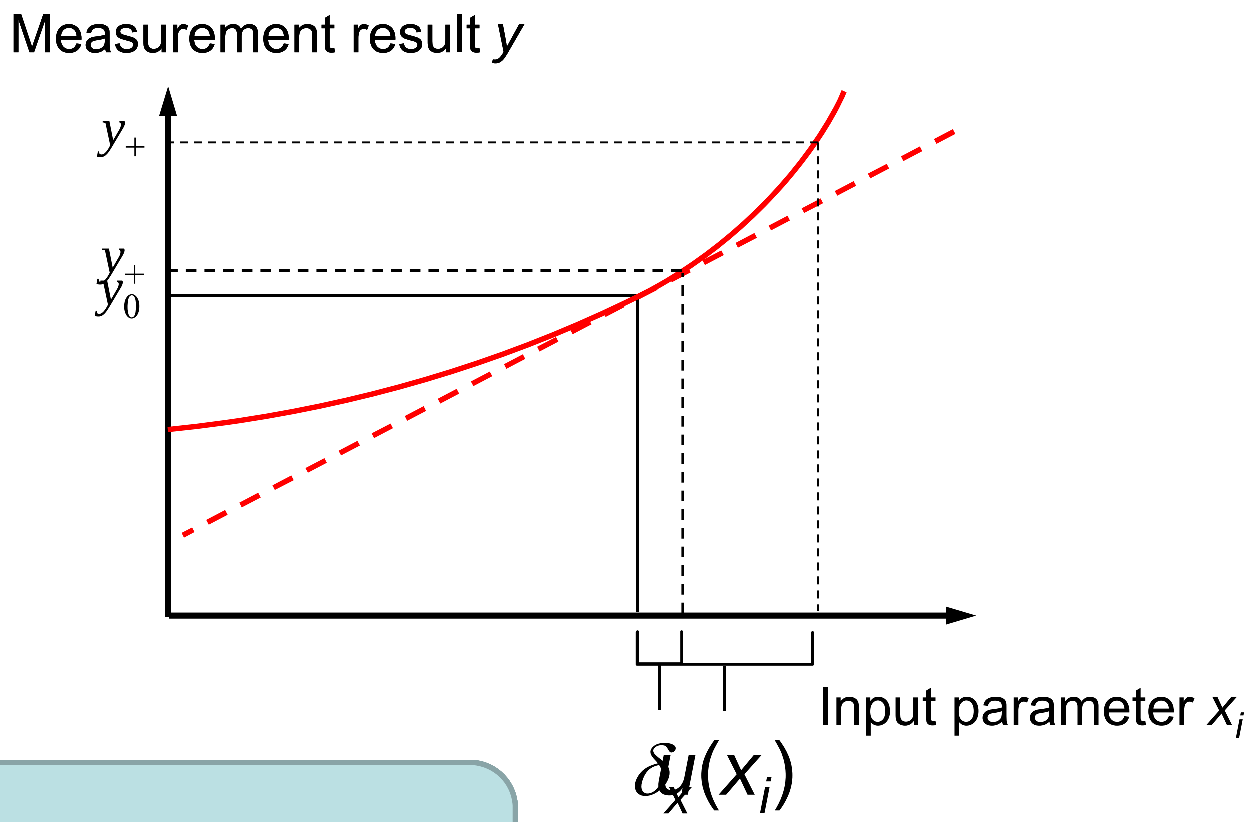
- Sampling has traditionally been managed through sampling guidance
  - Controlled sampling plans
  - Uncertainty on sample ‘as measured’
- Availability of UfS (sampling uncertainty) now permits treatment of sampling as part of uncertainty
- Is sampling an uncertainty, or a problem to manage?

# Combining uncertainties
# Recent theoretical options

# Combining uncertainties – The basic GUM approach



# Kragten's method
## - A spreadsheet approach




$$u_i(y) \approx y_+ - y_0$$

# Finite difference methods compared

## Finite difference 1st order

- Accurate gradient
- Faithfully reproduces 1st order GUM uncertainty
- Simple to calculate
- 1st order GUM is insufficient for highly non-linear cases
  - Needs 2nd and higher order

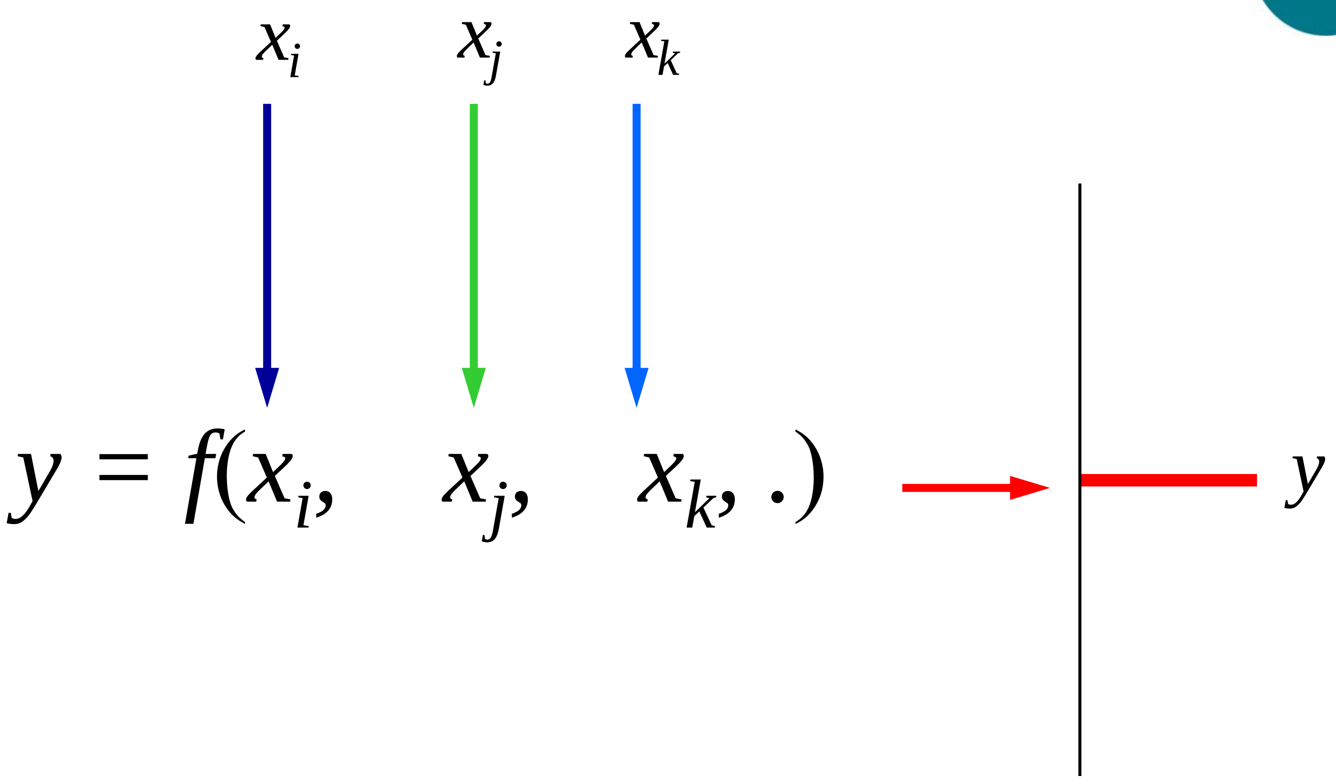
## Kragten

- Exact only for linear examples
- Does not reproduce 1st order GUM
- Simple to calculate
- Usually adequate for mild nonlinearity
- May be **better** for highly non-linear cases

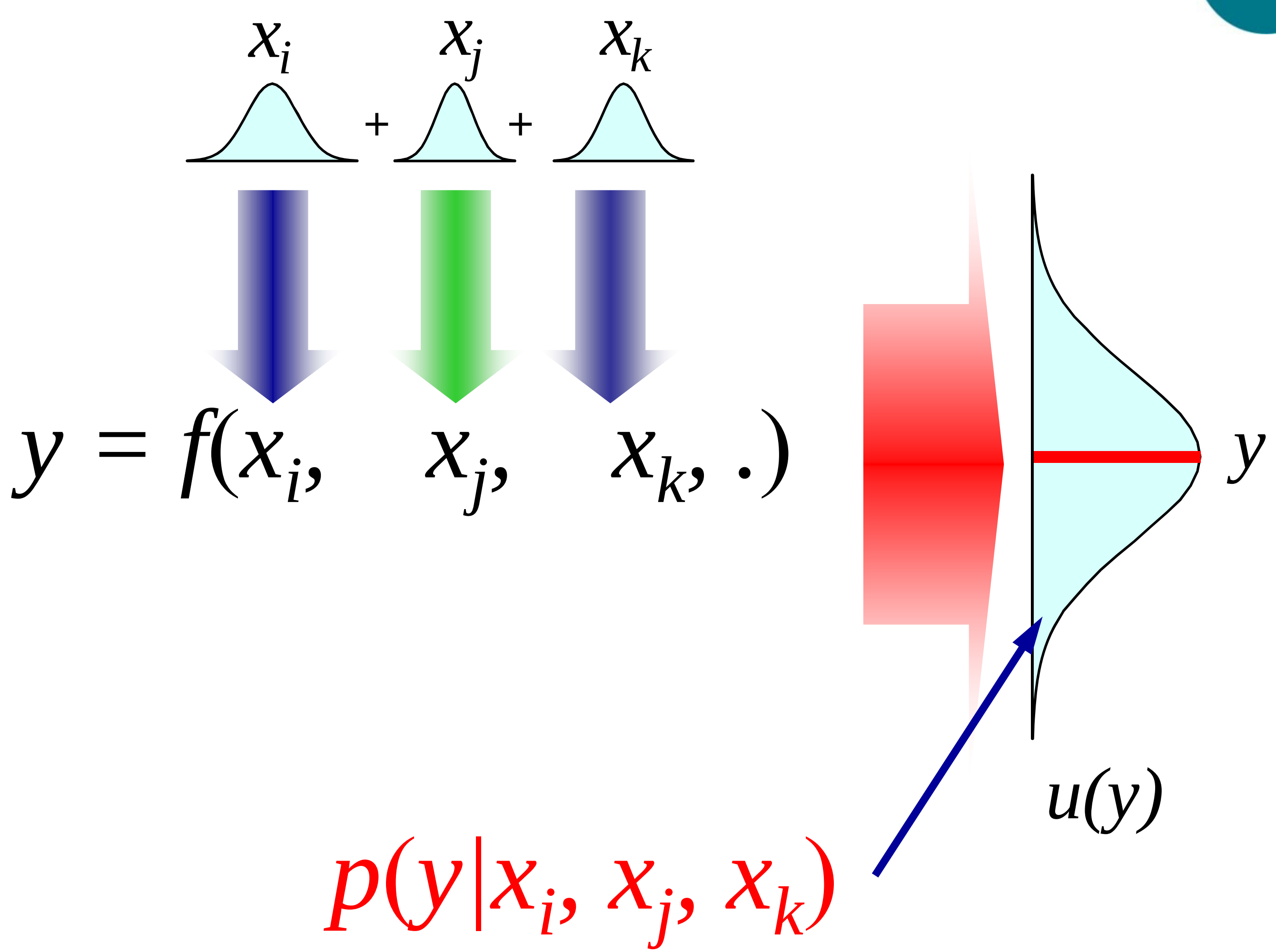
Both much simpler than manual differentiation

# ‘Supplement 1’ Monte Carlo
# A simulation-based approach

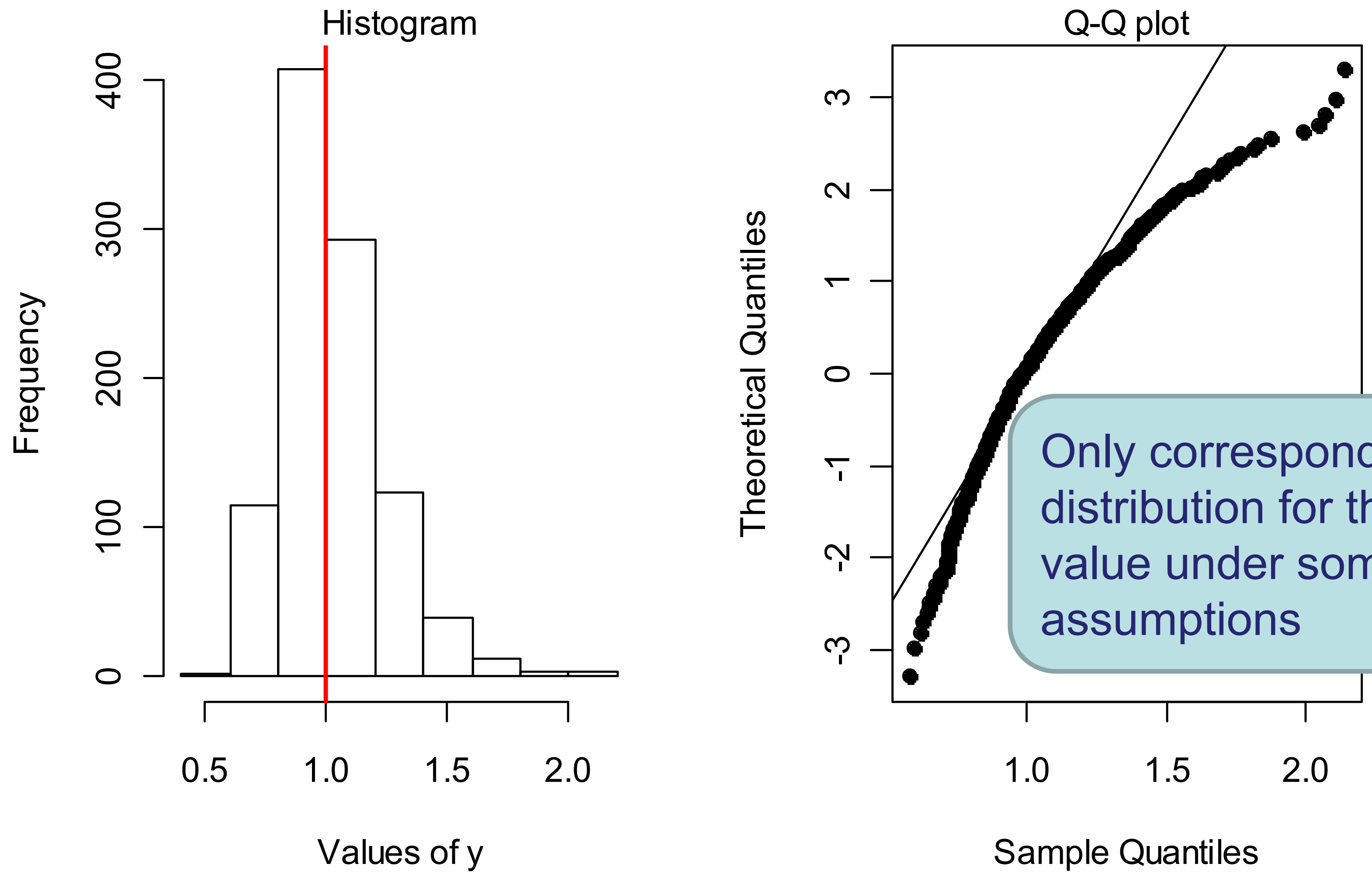
# Principle of simulation



# Principle of simulation



# MCS example
## *y* = *a*/(*b*-*c*) (999 replicates)




Only corresponds to distribution for the true value under some assumptions

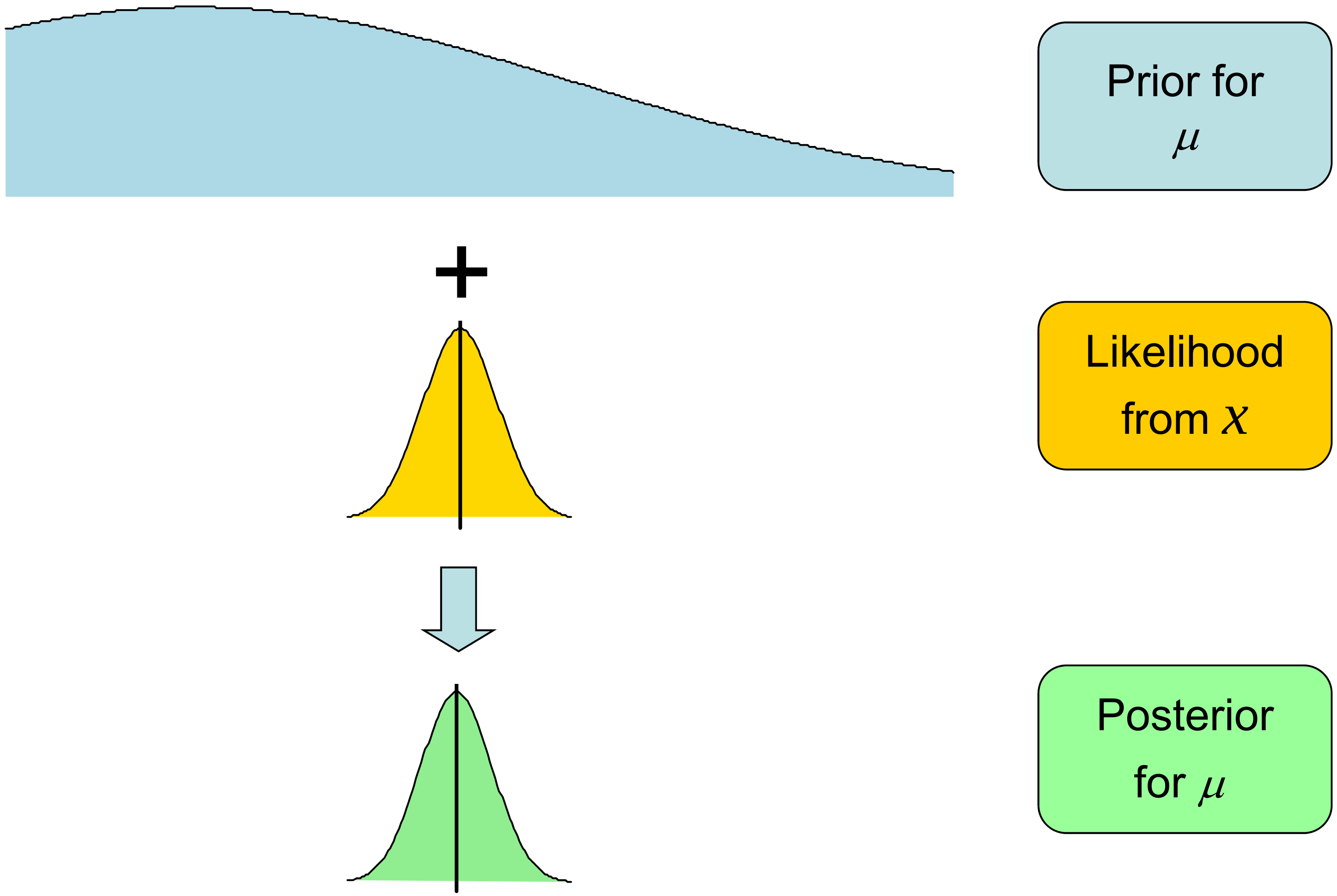
*Calculations carried out using metRology 0.9-4 (http://sourceforge.net/projects/metrology/)*

# Bayesian methods

- Considerable advances in statistics over the last 20-30 years
- Now reaching NMIs

- Start with a (usually uninformative) distribution for the value of the measurand
- Update based on observed data and uncertainties
- Integration (often numerical) provides a ‘posterior probability’ for the value of the measurand.

# Bayes applied to Measurement Uncertainty



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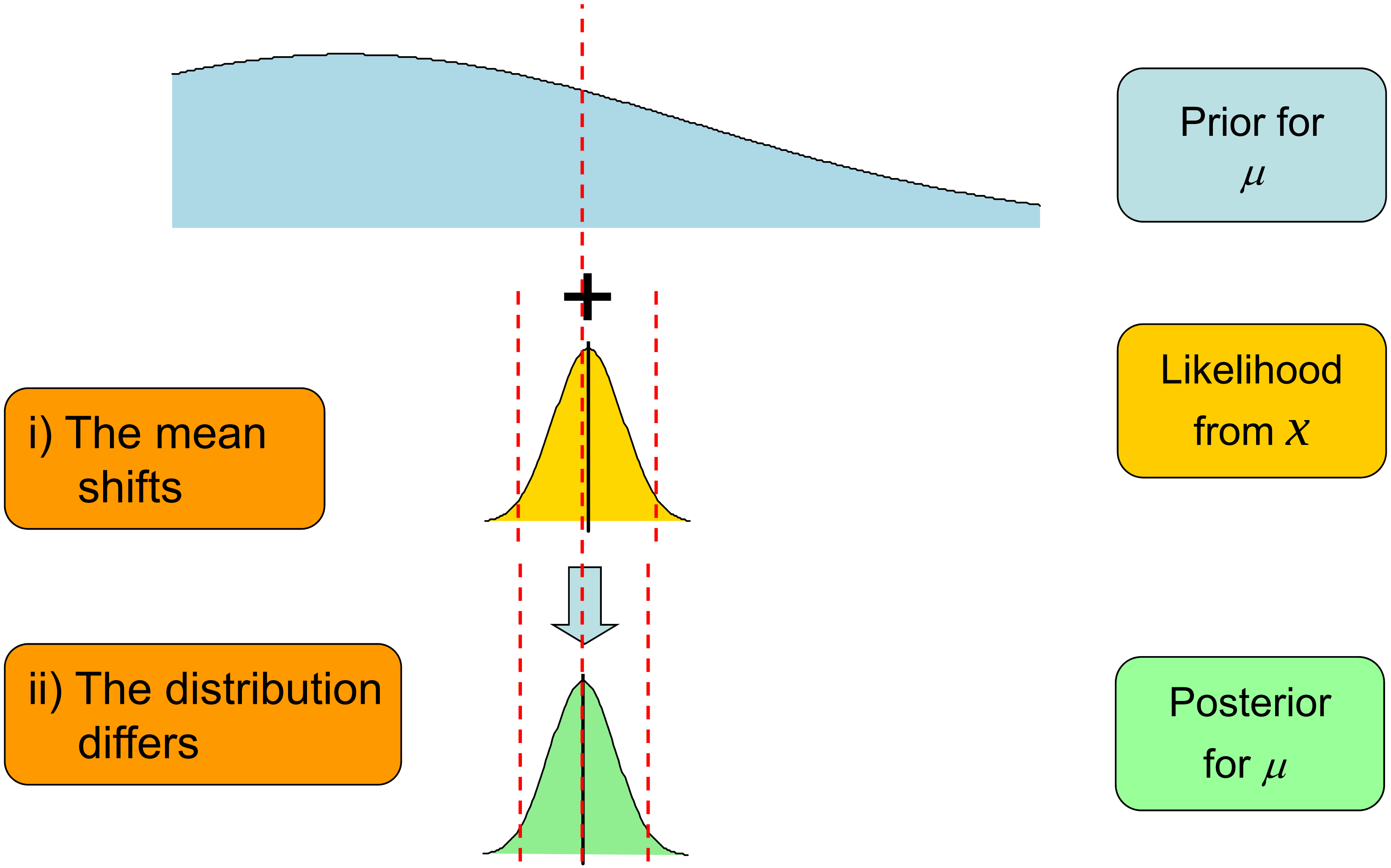
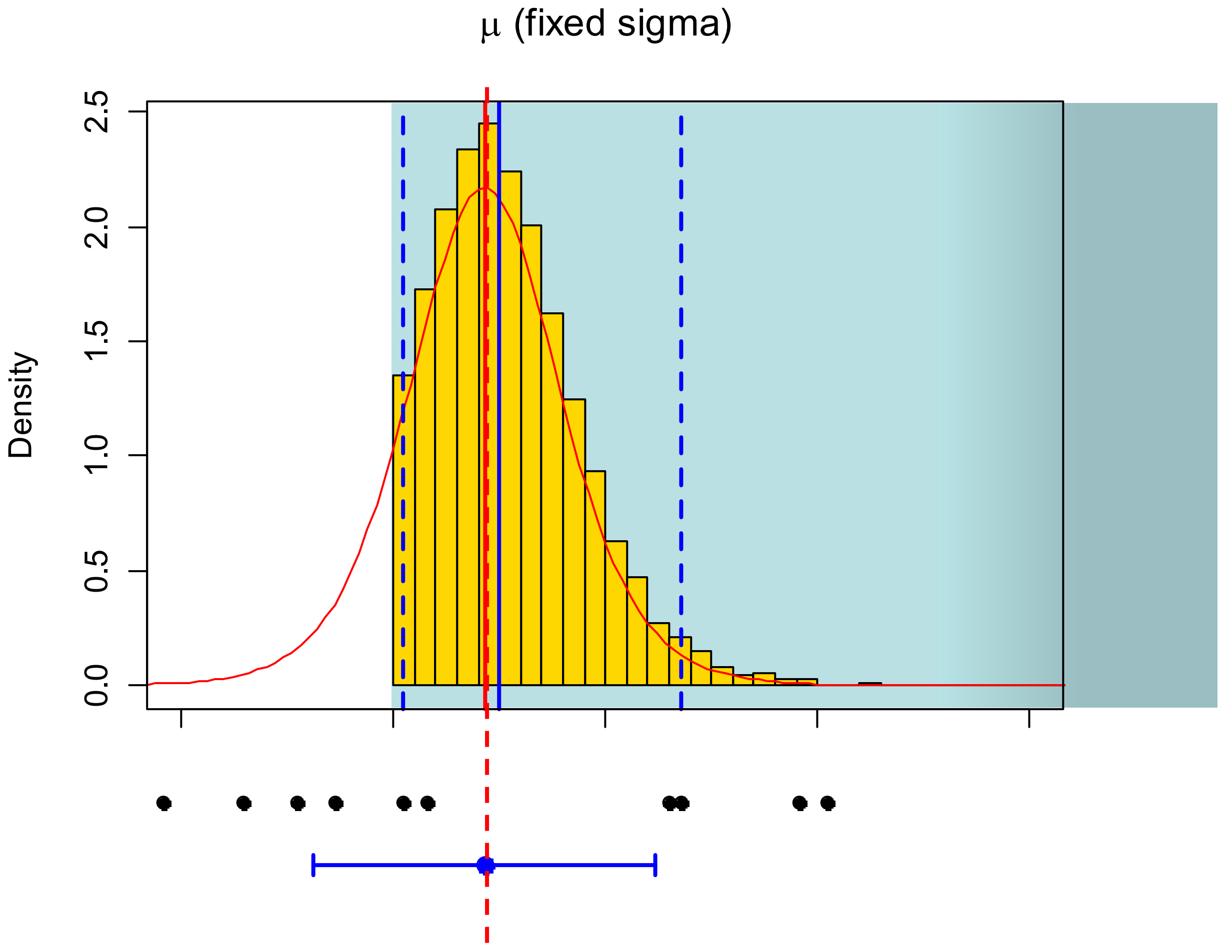
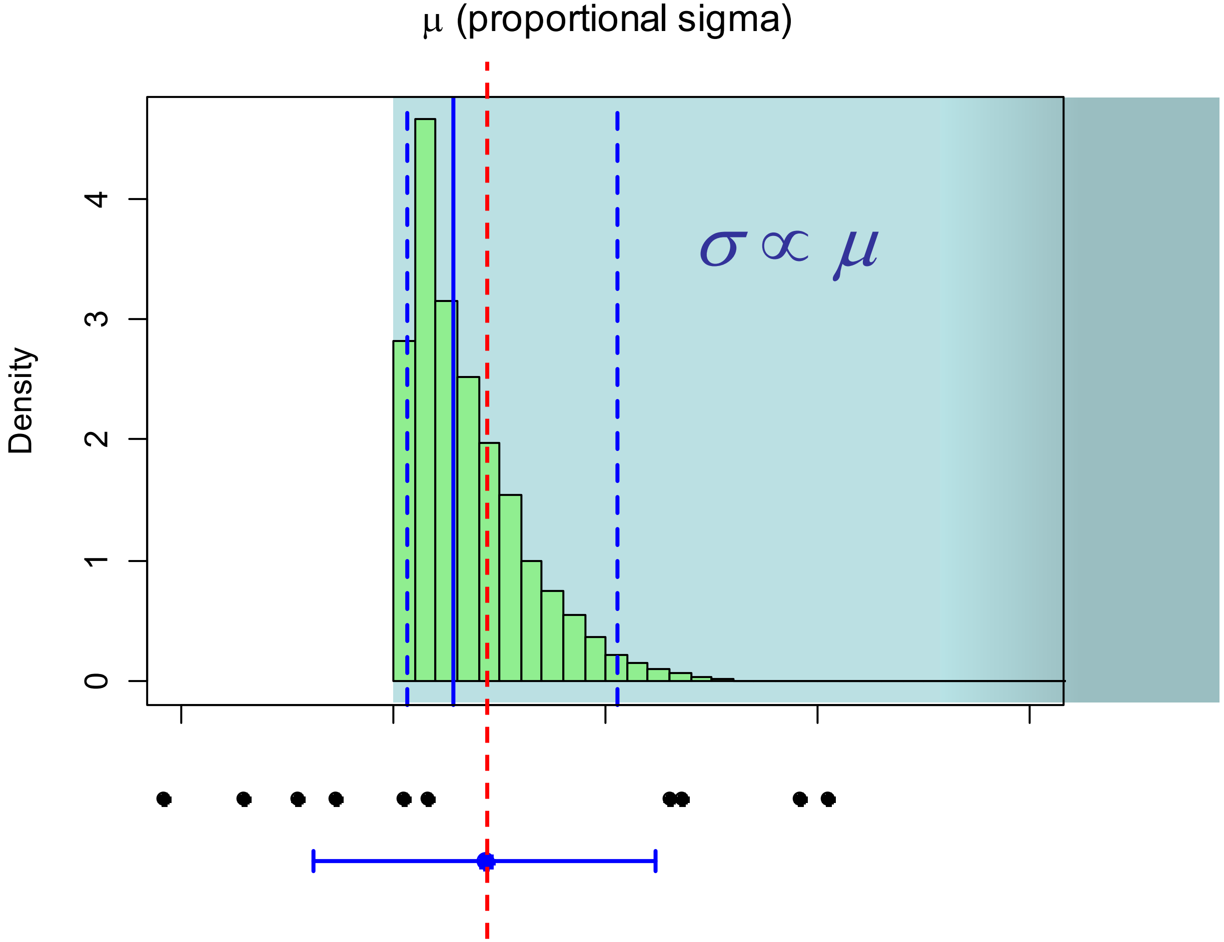


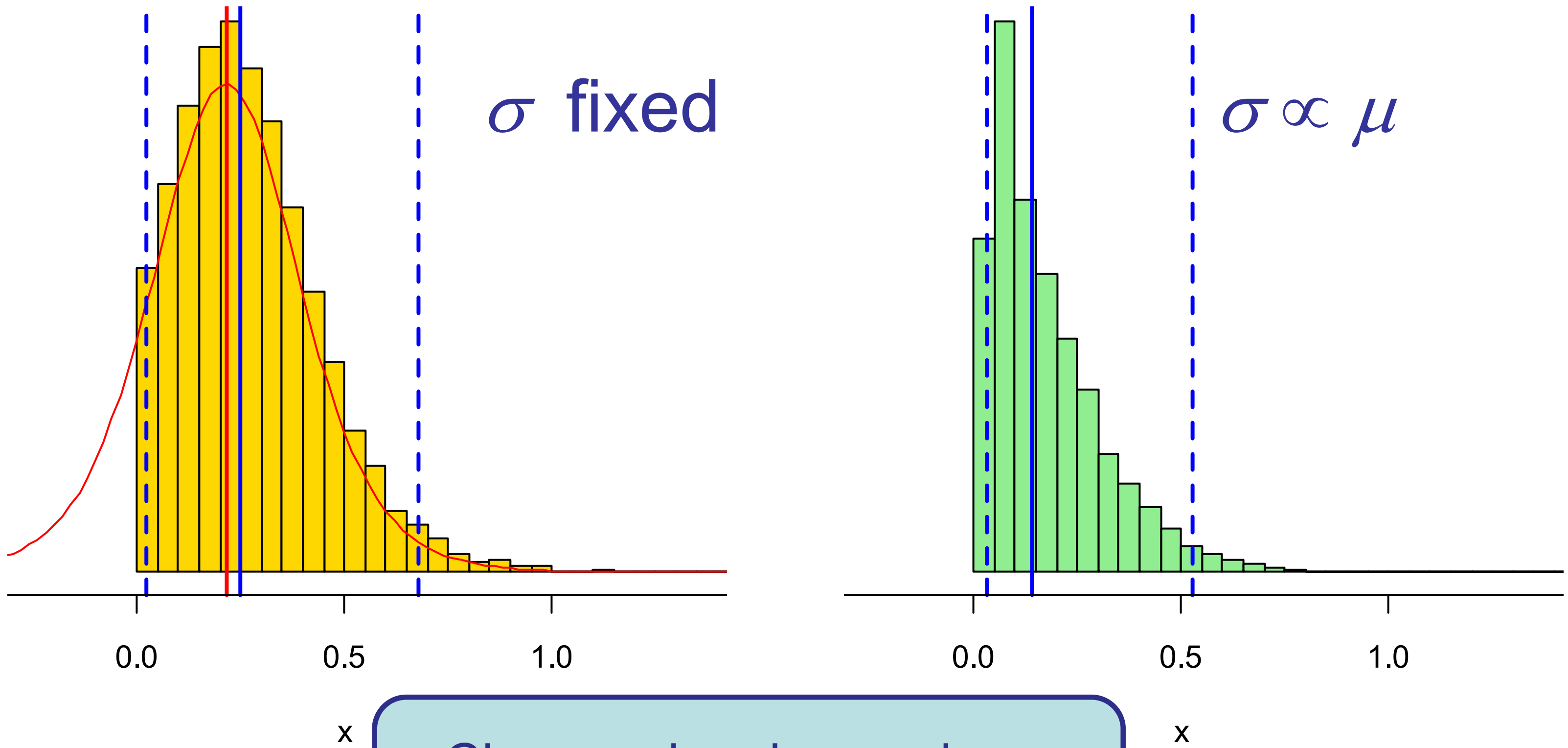
# Priors matter:
# i) Fixed standard deviation



# Priors matter:
# ii) Proportional standard deviation



# Priors matter in Bayesian analysis




Changes in prior can have unexpected consequences

# Current guidance

- Eurachem guidance covers uncertainty estimation for both analysis and sampling
- Covers basic GUM but also covers validation approaches thoroughly
- Uncertainty combination guidance includes recent simulation methods
- Guidance on uncertainty from sampling provides a simple methodology as well as describing modelling approaches

## What's missing?

- Still no firm consensus on handling uncorrected bias
- Very limited information about non-normality
  - Biological measurements; Large uncertainties (RSD > 0.3)
- Correlation
  - General advice only: arrange matters to eliminate the problem
- Sampling – an uncertainty or a problem to manage?
- 'Simple' but confusing problems
  - To root, or not to root …. when $\sqrt{n}$ is sensible; Independence
- Formal Bayesian treatments
  - The long term direction of JGCM?

# Looking forward

- Chemical testing laboratories are probably content with uncertainties based on validation and interlaboratory study data
- Increasing interest in reporting uncertainties in proficiency tests
- Simplified Bayesian approach likely in future GUM implementation
  - Small degrees of freedom ($\leq 2$) for some components of uncertainty will be a problem for chemists
- Full Bayesian treatments will take time to understand
  - Intuition is a poor guide to sound priors

# Summary

- Much done

- Probably more to do
  - More short guidance on ‘simple but confusing’ problems
  - Adapting to future JCGM guidance
  - Bayesian approaches – probably needs long term development
  - Policy decisions on sampling