Eurachem
A Focus for Analytical Chemistry in Europe

Eurachem/Eurolab Workshop
Uncertainty from sampling and analysis for accredited laboratories

Applications of UfS estimation across a range of sectors

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19-20 November 2019
BAM Headquarters, Unter den Eichen, Berlin, Germany

Content of presentation

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- Overview of application of the Guide on UfS since first edition in 2007

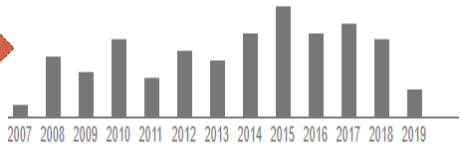
Examples from literature:

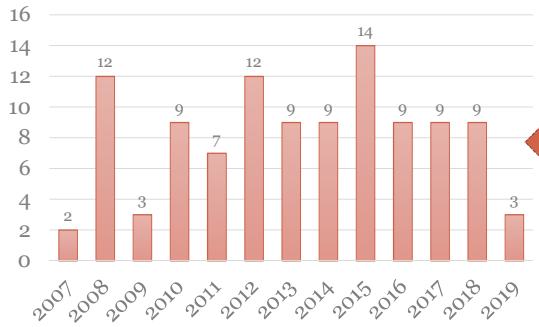
- Who and how researchers apply methods of UfS recommended in the Guide?
- Criteria for choosing method approach?

Citations of the Guide since 1st Edition

3

2007-2019: 153 citations
Source: Google Scholar





107 citing documents accessed for this presentation

Accred Qual Assur (2007) 12:503–513
DOI 10.1007/s00769-007-0279-0

REVIEW PAPER

Uncertainty from sampling, in the context of fitness for purpose

Michael H. Ramsey · Michael Thompson

Environ Geochem Health (2009) 31:205–217
DOI 10.1007/s10653-008-9211-8

REVIEW PAPER

Uncertainty in the assessment of hazard, exposure and risk

Michael H. Ramsey

Review papers

Vol. 34 – N° 3 | 09 10 | p. 293–304

GEOSTANDARDS and GEOANALYTICAL RESEARCH

New Approach to Geochemical Measurement: Estimation of Measurement Uncertainty from Sampling, rather than an Assumption of Representative Sampling

Michael H. Ramsey and Katy A. Boon

Overview papers on development of new approaches/ concepts

Vol. 40 – N° 4 | 12 16 | p. 571–581

GEOSTANDARDS and GEOANALYTICAL RESEARCH

Appropriate Sampling for Optimised Measurement (ASOM), rather than the Theory of Sampling (TOS) Approach, to Ensure Suitable Measurement Quality: A Refutation of Esbensen and Wagner (2014)

Michael H. Ramsey

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Scope of research in presented examples

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- Uncertainty estimation method development – adaptation of Guide's methods to specific sampling media
- Use Guide's methods to confirm that data are fit-for-purpose in supporting their interpretation.
- Regulatory-Organisational Documents

Application of UfS methods by sector

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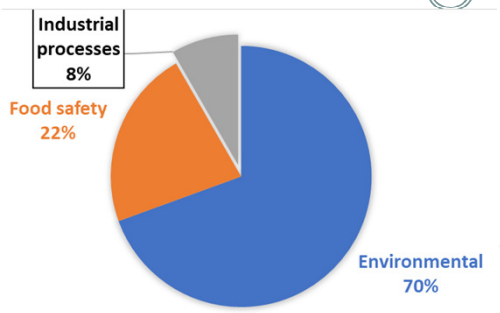
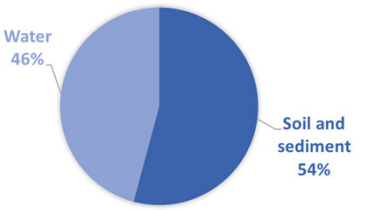
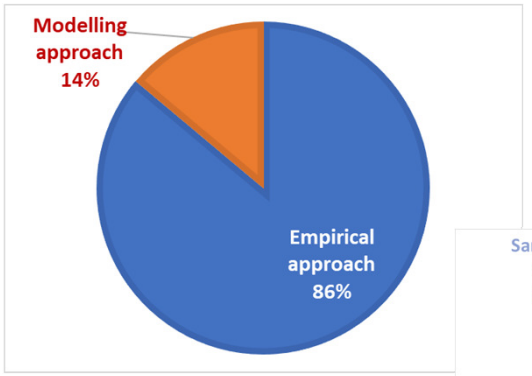


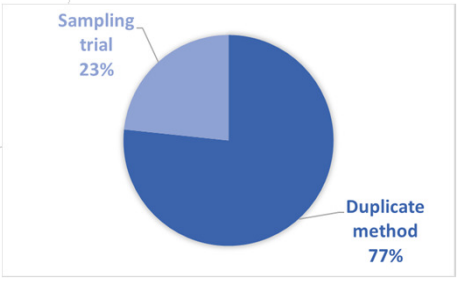


Based on 36 research paper Case studies

Method approaches

7





Applications of Empirical Method

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Agricultural soil

- SOILSAMP project (Italian Environmental Protection Agency)
- Set up of agricultural area as a **reference site** suitable for
- performing soil sampling inter-comparison exercises.
- The reference site was characterized for trace element content in soil, in terms of the spatial and temporal variability of their mass fraction.
- The reference site of Pozzuolo del Friuli, characterized for element mass fractions, is available to researchers and scientific institutions concerned with this issue.
- Increasing interest in the harmonization of sampling procedures for environmental monitoring and control, as well as for more detailed information on sampling quality

De Zorzi et al., 2008 Applied Radiation and Isotopes 66, 1588– 1591

Three different sampling devices were applied in an **agricultural area** using the same sampling protocol.
Metal mass fractions in the collected **soil samples.**
The approach based on the **use of variogram** parameters leads to uncertainty values of the sampling component in agreement with those estimated by **replicate sampling** approach

Table 3
Comparison between standard uncertainty from sampling calculated by variogram parameters and applying the replicate approach

	Empirical approach	
	Variography u_s	Replicate $u_{s\text{-SOILSAMP}}$
Sampling standard uncertainty (mg kg^{-1}) (Cr)	5.9–7.5	3.7
Sampling standard uncertainty (mg kg^{-1}) (Sc)	0.22–0.43	0.20
Sampling standard uncertainty (mg kg^{-1}) (Zn)	2.5–3.6	2.8

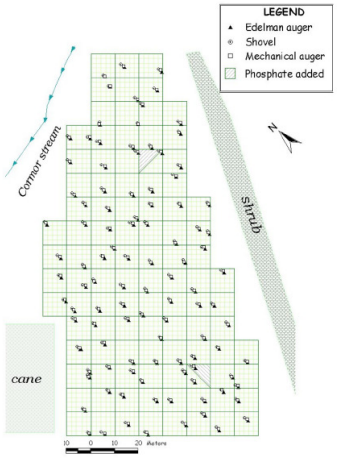

Fig. 1. Sampling design by three sampling devices in the comparative sampling.

De Zorzi et al., 2008 Chemosphere 70, 745–752

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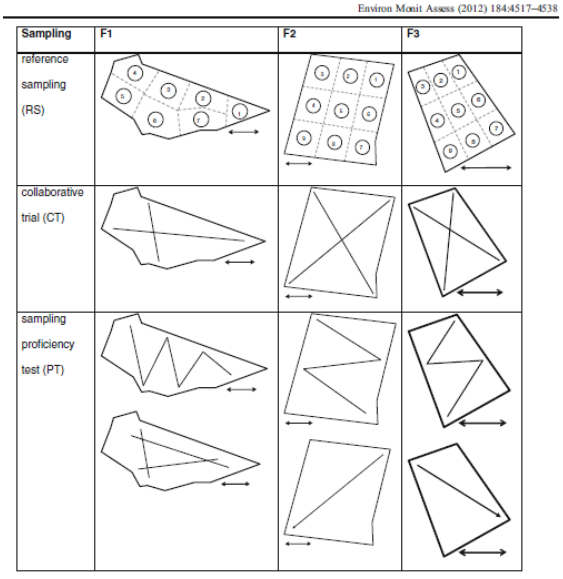
To elucidate the magnitude and relative proportions of uncertainty components for the metals As, B, Cd, Co, Cr, Mo, Ni, Pb, Tl and Zn in three **arable fields** of different field-scale heterogeneity, based on a **collaborative trial** (CT) (standardized procedure) and two **sampling proficiency tests** (PT) (individual sampling procedure). To obtain reference values and estimates of field-scale heterogeneity, a detailed reference sampling was conducted
Buczko et al. 2012



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XRF measurements

A **column of soil**, excavated from a **contaminated landscape** was evaluated by means of **X-ray fluorescence** analysis. The required measurement uncertainty components caused by both the sampling procedure and chemical analysis were empirically estimated using a nested sampling design (duplicate method). The evaluation of the estimated variance components in terms of the percentage of total variance confirmed **fitness for purpose** for the method used. ***Morgenstern et al. 2008***

Capability of a XRF Method for Monitoring the Content of the Macronutrients Mg, P, S, K and Ca in **Agricultural Crops**
The required estimates for measurement uncertainties were provided by the application of the duplicate method to the plant material taken from an adequate number of cultivated targets (lysimeter trial).
Morgenstern et al. 2010

Ex-situ hybrid methodology, two analytical techniques were complimented, namely inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF) to measure Pb and Zn in **ex-shooting range park area**
Urrutia-Goyes et al. 2017

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Quantifying Heterogeneity of Small Test Portion Masses of **Geological Reference Materials** by Portable **XRF** Spectrometry.

Two components of variance are of interest, that due to heterogeneity within the pellets, and that due to analytical repeatability between duplicated analyses.
Rostron and Ramsey 2016

SdAR Reference Materials - Uncertainty Supplement

Uncertainty estimates for evaluating the significance of bias of PXRF measurements using the SdAR-H1, SdAR-M2 and SdAR-L2 reference materials

Annex to Reference Material Data Sheets
SdAR-H1 Metalliferous sediment
SdAR-M2 Metal-rich sediment
SdAR-L2 Blended sediment

Peter Rostron and Michael H. Ramsey
University of Sussex
January 2017

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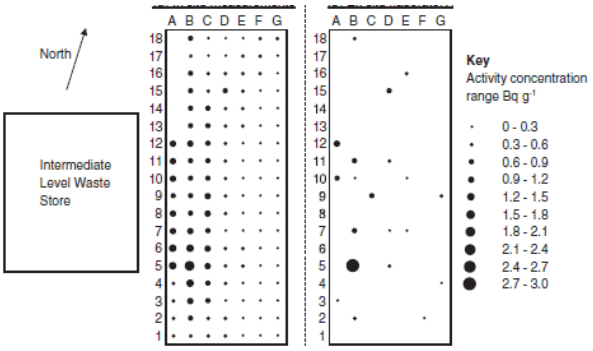
Radioactivity measurements

A method has been devised to calculate the optimised counting time, detector height and measurement spacing required for the detection of **radioactive particles** at pre-defined probabilities of false positive and false negative errors, when using a static **gamma detector in -situ**

The random component of analytical uncertainty in situ > the ex situ measurements,

- Contamination by the target radionuclide was found to be heterogeneous over small spatial scales.
- This resulted in significantly higher levels of random sampling uncertainty in individual ex situ measurements



Rostron et al, 2014

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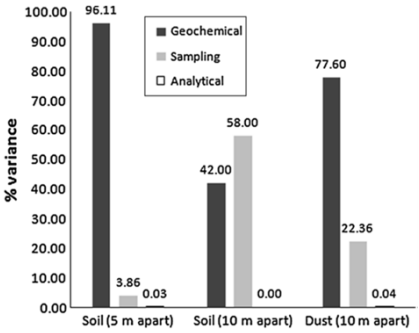
Mining areas

Duplicate method- Information on the degree of spatial heterogeneity of Pb. Robust ANOVA results to compare analytical and sampling contribution **Soil** sample duplicates separated by 5 and 10 m, and **house dust** duplicates separated by 10 m

Argyraki 2014



Assessing soil sampling uncertainty in heterogeneous historic metal ore mining sites Eighteen duplicate, **composite soil samples** from heterogeneous remote historic metal ore mining sites in Poland analyzed twice for trace elements.
The sampling uncertainty [expressed as the relative standard deviation srsamp (%)] was computed using three different methods: ANOVA, RANOVA and range statistics – **Effect of non-normal distribution noted**

Dołegowska et al. 2015

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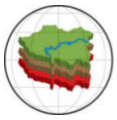
Wide scale studies- geochemical mapping

BGS project- **Urban geochemical mapping** studies: how and why we do them
G-BASE project- reference to the "depth effect"
Uses duplicate method
Johnson and Ander 2008



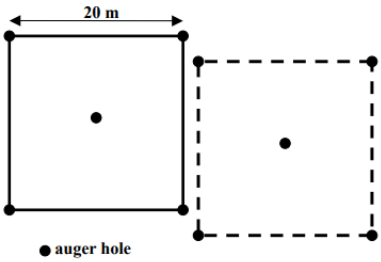


Figure 12-1: Plan of composite auger holes for collecting a soil sample (dashed square represents adjacent duplicate sample)

! The Duplicate method was also adopted in the Eurosurveys GEMAS project and the Sampling manual of the IUGS-Global Geochemical Baselines (in preparation)

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Suspended material in river water

Environmental radioactivity study- aquatic environment of Po river (Italy), downstream of the deactivated Italian nuclear power plant of Caorso.

to estimate the **measurement uncertainty including sampling**, derived by the approach implemented by Ramsey for soil investigations.

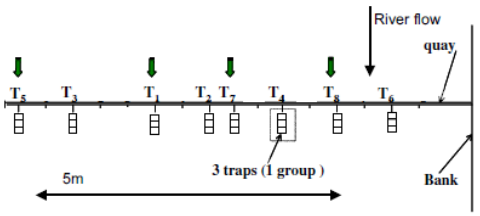

Fig. 3. Scheme of the sampling apparatus as installed in the Po River (Italy). T_i = group of traps number *i*.

The duplicate methodology has been applied to estimate the measurements uncertainty (sampling and analyses) of 137Cs activity concentration (Bq/ kg) and total carbon content (%) in **suspended particles** sampling in a freshwater ecosystem.
Barbizzi and Pati 2008

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Sea water monitoring

Figure 1 shows the nested and balanced experimental design that may be applied to 12 sampling targets. A

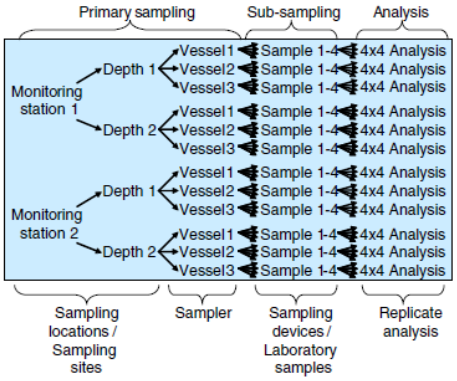
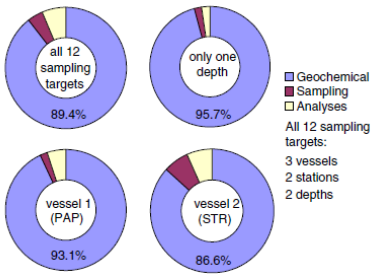


Fig. 1 Experimental design scheme of the organized collaborative sampling trial

Gluschke, 2008

Collaborative trial in sampling in the Baltic Sea in the framework of quality assurance in the German marine monitoring programme for the North Sea and the Baltic Sea.
Measuring nutrients in sea water



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Measurement uncertainty associated with shipboard sample collection and filtration for the determination of the **concentration of iron in seawater.** Seawater samples collected in the South Atlantic during the **GEOTRACES GA10 cruise**

Application of robust ANOVA to the deep open ocean samples showed that contributions to the total variance were :

- 0% from the different sample collection and filtration strategies,
- 42% from the sub-sample precision and
- 58% from between sub-sample measurements

Clough et al. 2016

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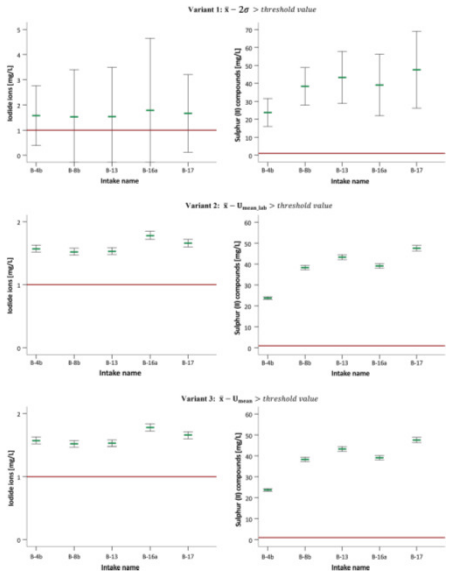
Groundwater research

Application of duplicate method and probabilistic assessment of comparison with threshold values – **medicinal qualities of groundwater** from the Busko-Zdroj area (Poland)

Consideration of analytical bias

Wator et al. 2016



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Baseline groundwater **monitoring for shale gas extraction**: definition of baseline conditions and recommendations from a real site (Wysin, Northern Poland)

It is assumed that measurement uncertainties are constant during the entire monitoring programme. Therefore, uncertainties are estimated by using all **duplicates collected over the course of the 2-year** monitoring programme (representing 10% of the collected samples).

A total of five duplicate pairs were available

Montcoudiol et al. 2019 Acta Geophysica 67:365–384

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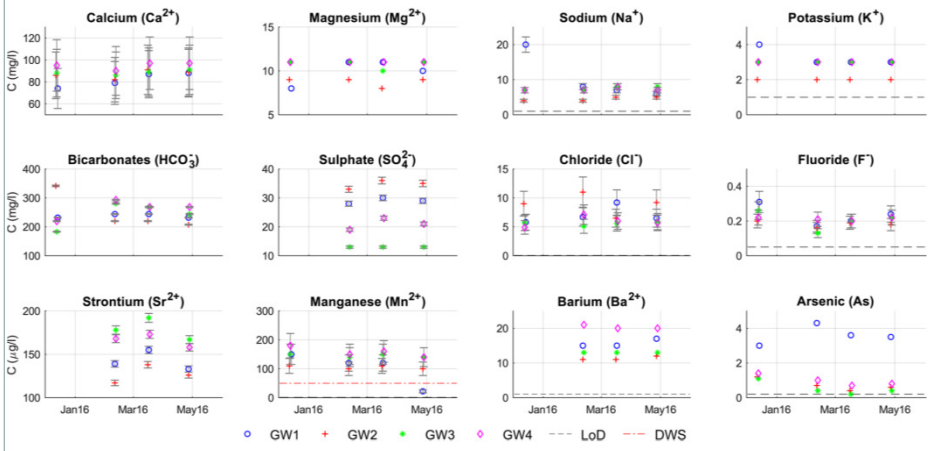
Seasonal variation of concentrations with error bars based on duplicate method



Montcoudiol et al. 2019 Acta Geophysica 67:365–384

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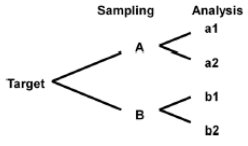
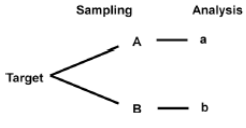
River water monitoring

Long-term Environmental Research Monitoring and Testing System (OPE), - Estimating sampling and analysis uncertainties to **assess the fitness for purpose** of a water quality monitoring network

Table 2 Detailed costs of Design A and Design B

	Design A	Design B
Monitoring cost for the water quality variability study	58 600 €	58 600 €
Design for the duplicate method of the validation study	Double-split design 	Single-split design 
Number of additional analyses for the validation study	3	1
Number of water quality parameters and chemical species selected	14 + 4 metals and 4 pesticides (triazines and phenylureas)	13
Validation study cost	52 000 €	8 800 €
Total cost	110 600 €	67 400 €
Ratio of validation study cost to total cost	47 %	13 %

Guigues et al. 2015 *Accred Qual Assur*

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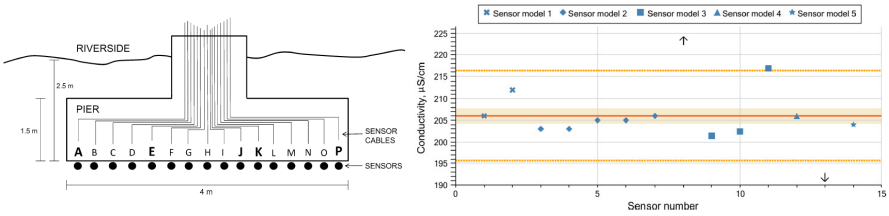
First **proficiency test** (PT) in Finland for field measurements of temperature, conductivity, dissolved oxygen concentration, oxygen saturation and pH value in **river water**.
Field sensors used

For the evaluation of performance of each participant, z scores were calculated, allowing between 3 % and 8 % deviation from the assigned value.

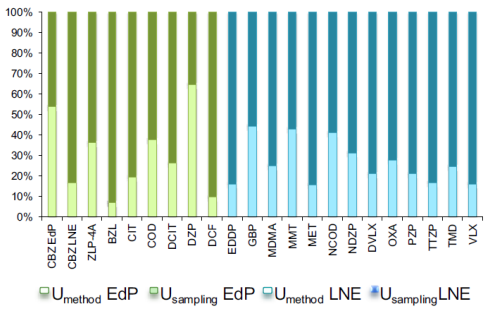


Naykki et al. 2014 Accred Qual Assur (2014) 19:259–268

Development and implementation of a Di-MS based method with full uncertainty estimate to achieve measurement of pharmaceutical residues in natural waters
Sampling and analysis trial involving 2 labs- sampling duplicates collected

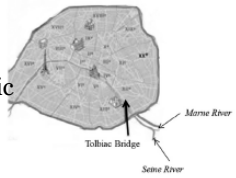
- It reemphasized that the main contribution to the uncertainty of measurement is linked to sampling uncertainty.
- For end-users 'x±U', - interval as including the range of values attributable to the concentration at the sampling station at a given time.

Significance of measurand definition

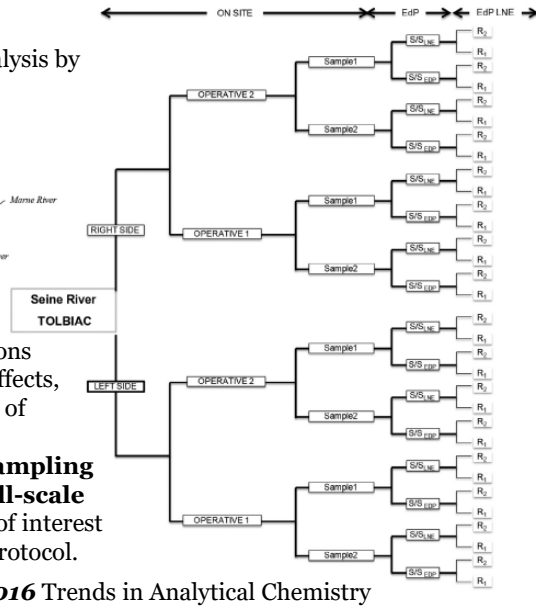


Lardy-Fontan 2015 17 International Congress of Metrology

- Duplication of sampling and analysis by two labs
61 compounds
17 different Chemotherapeutic classes



Seine River



Duplicate samples:
collected after permitted variations sampling protocol – bank side effects, sampling operatives, replication of sampling effects – that reflect the **ambiguity in the sampling protocol** and the effect of **small-scale heterogeneity** of the analytes of interest on the implementation of that protocol.

Lardy-Fontan et al. 2016 Trends in Analytical Chemistry

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Sampling trial by French River Basin Agencies (RBAs), and the French Ministry of Ecology. - first national attempt to improve knowledge of the effect in **natural river waters** of sampling activity undertaken as part of regulatory monitoring.14 sampling teams that took part in the trial
- results obtained for non-field parameters
- solutions that we developed to overcome the difficulties caused by a **storm the day before the trial** (unexpected event adding to variation).

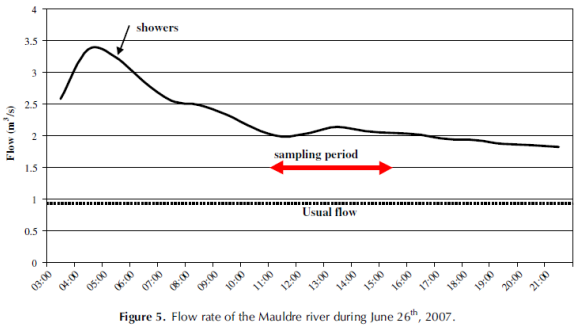

Figure 5. Flow rate of the Mauldre river during June 26th, 2007.

Sampling is influenced by many factors, including weather conditions, which cannot be predicted. Sampling comparability is indeed more difficult to improve than analytical comparability.

Strub et al. 2009 Trends in Analytical Chemistry, Vol. 28, No. 2

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EU FP6 **project BRIDGE** (Background cRiteria for the IDentification of Groundwater thrEsholds)
Research for Policy Support
Deliverable 16: Summary Guidance and Recommendations on Sampling, Measuring and Quality Assurance.
(2006)

Ability of the given monitoring site to detect the preset level of deterioration of groundwater quality (e.g. 20%) with the assumed confidence level (e.g. 95%). This can be reached by assessment of measurement uncertainty in the framework of **empirical approach**.

EU-WFD Guidance Document No: 25
Guidance on chemical monitoring of sediment and biota under the Water Framework Directive (2010)

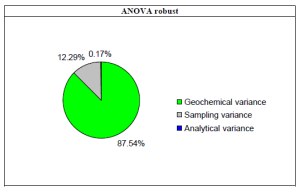
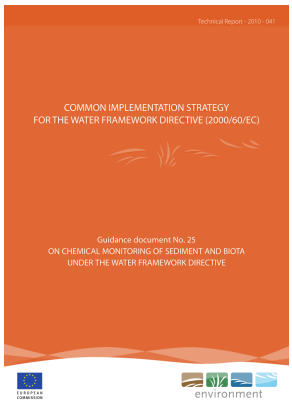


Figure A2.5. Relative contributions of sampling and analytical variances to the total variance for Mn.



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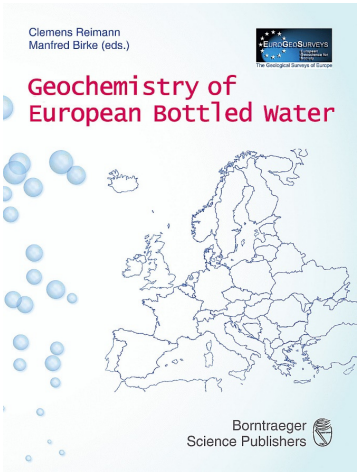
Use of measurement uncertainty in a probabilistic scheme to assess compliance

Hierarchical nested balance design for the collection of random primary duplicate water samples, and their replicate analyses, is described, and the use of **robust analysis of variance** to estimate measurement uncertainty.

Development of four probabilistic categories for the classification of element concentrations in bottled water with respect to legislative standard values.

Demetriades, 2010



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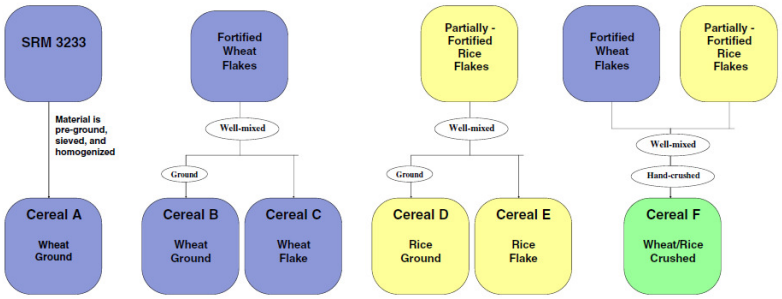
Food safety

NIST study - effects of material granularity and sample processing techniques on measurement variability (precision) and performance relative to the NIST assigned values (bias) and to the other participants (concordance). Participants were asked to determine the mass fractions of Ca, Fe, and Zn, in mg/kg, in six **breakfast cereal samples**.

The relative variability of triplicate measurements for Ca, Fe, and Zn in each of the six materials was assessed and compared with the sample processing information provided by each laboratory.



Wood et al. 2013 Anal Bioanal Chem (2013) 405:4569–4578

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Empirical data- fit into model uncertainty

- The sampling uncertainty for **pesticide residues in carrots, parsley leaves** and selected medium size crops was estimated with simple random sampling by applying range statistics.
- Results indicated that taking a minimum of 6 replicate samples from at least 8–12 lots is recommended to obtain a relative 95% range of sampling uncertainty within 50%.
- CV values calculated from the samples concurred with the theoretically expectable ones based on the central limit theorem.

Example of using empirical data to test the model uncertainty,
e.g. fill the information gap by conducting field trials in carrot and parsley leaves representing root vegetables and vegetables with small leaves, respectively,
- to estimate the uncertainty of sampling for such crops, by applying simple replicate random sampling and duplicate sampling.

Farkas et al 2014 J. Environmental Science and Health, Part B, 49, 1–14

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BIOTRACER EU project

Automatic and manual sampling for ochratoxin A **(OTA) in barley grain** was compared under industrial conditions considering sampling uncertainty practical and technical aspects. A nested experimental design and ANOVA was used to estimate variance components from sampling, sample reduction, sample preparation and analysis.

- Manual sampling resulted in a high sampling uncertainty and OTA concentrations in aggregate samples ranged from 2 to 80 mg/kg.
- By automatic sampling the uncertainty arising from nugget effects and spatial distribution was practically eliminated.

Andersson et al. 2011 Food Additives and Contaminants Vol. 28, No. 8, 1066–1075

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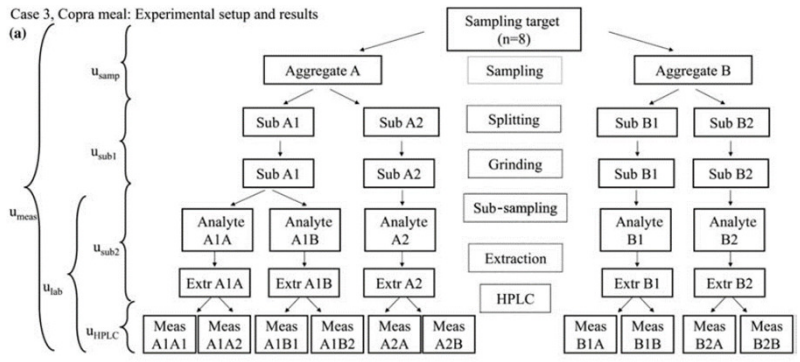
BIOTRACER EU project- Uncertainty from sampling in measurements of aflatoxins in animal feedingstuffs: application of the Eurachem/CITAC guidelines
The applicability of the duplicate method as a tool for verifying sampling plans for **mycotoxins** was assessed in three case studies with aflatoxin B1 in animal feedingstuffs. An important part of this work was to compare the applicability of **robust statistics against ANOVA on log10-transformed data** for estimating and
presenting measurement uncertainty from sampling



Reiter et al. 2011 Analyst, 136, 4059

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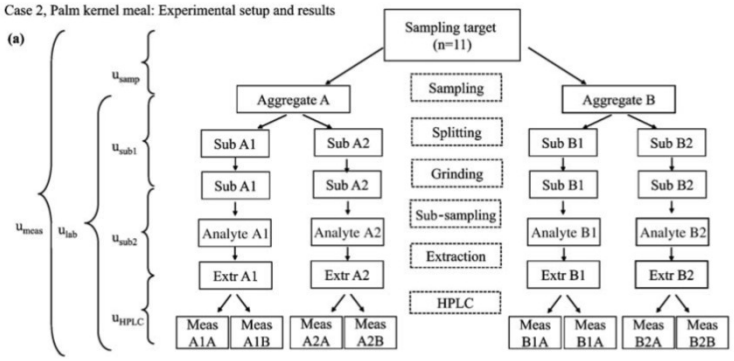
Case 2, Palm kernel meal: Experimental setup and results

(a)



(b)

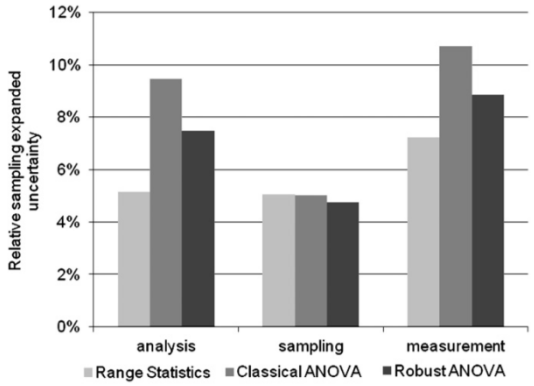
Palm Kernel Meal (x_M=0.30 µg/kg)	ANOVA		RANOVA		ANOVA(log)				
Source of variability	U_{rel}[a] (%) (p=0.05)	%var[b]	U_{rel}[a] (%) (p=0.05)	%var[b]	SD[c] (log_{10}(µg kg^{-1}))	%var[d]	Coverage interval (%) (p=0.05) Upper[e]	Lower[f]	Lin-log U_{rel} (%) (p=0.05)
Sampling (u_s)	47	63	50	69	0.108	64	+65	-39	51
Laboratory (u_{lab})	36	35	33	30	0.081	36	+45	-31	38
HPLC (u_{HPLC})	8	1.7	7	1.3	0.016	1.4	+7.6	-7.1	7.3
Measurement (u_{meas})	60		61		0.136		+87	-46	64

[a](100 * 2*u/x); [b](u^2/u_{meas}^2); [c]sd(log(ug/kg)); [d](SD^2/SD_{meas}^2); [e]100x(10^U-1); [f]100x(1- 10^{-U})

Research in Fuel quality

- The **sulfur mass content** is a critical fuel quality parameter associated with automotive **diesel specifications** and is often used for identifying fuel cross contamination or fuel adulteration incidents.
- Duplicate method applied in sampling fuel
- The results were treated using classical ANOVA, robust ANOVA and range statistics.

The three methodologies gave statistically different estimates



Theodorou et al. 2013
Talanta 105 360–365

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Applications of Modelling Method

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Food chemistry

- Develop an analytical method to assure the geographical origin of Styrian **pumpkin seed oil** by using REE analysis.
- Sampling recognized as dominating component contributing to the combined measurement uncertainty
- Effect of primary sample, sub-sample and the conditions on the field

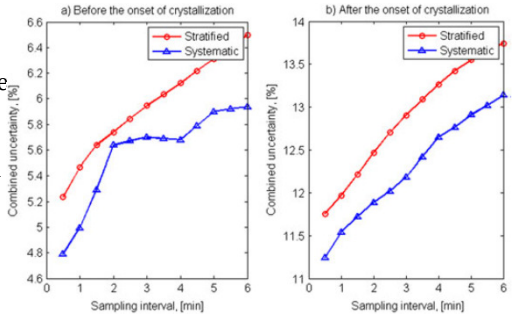
like clime, ripeness of the pumpkin seeds, homogeneity of the earth etc., physical sample preparation (milling, selection of a test portion) were considered.

- An average combined measurement uncertainty (uc) of all REE was calculated to be 35 rel% with the pumpkin ripeness and the sampling in field as largest influence quantities.

Joebstl et al. 2010

Crystallization process

Application of sampling theory to optimize sampling frequency of specta signals. Evaluation of variation in dynamic processes via online spectrometers as example
An adequate sampling interval can be determined
for spectral measurements when utilizing a **multivariate extension of variography** by applying score vectors as independent sources of uncertainty.
This approach is illustrated with a crystallization process continuously followed with an attenuated total reflectance Fourier transform infrared instrument.
Kohonen et al. 2012



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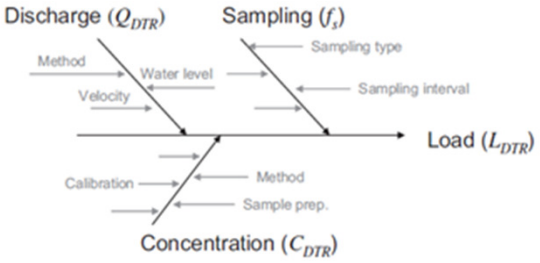
Drugs in wastewater



Assessment of total uncertainty in cocaine and benzoylecgonine wastewater load measurements

(i) a generic model-based procedure to investigate the influence of the sampling scheme on the uncertainty of observed or expected drug loads,

(ii) a comparative analysis of two analytical methods (high performance liquid chromatographyetandem mass spectrometry and gas chromatography mass spectrometry), including an extended cross-validation by influent profiling over several days, and

(iii) monitoring COC and BE concentrations in WW of the largest Swiss sewage treatment plants. ***Mathieu et al. 2011***

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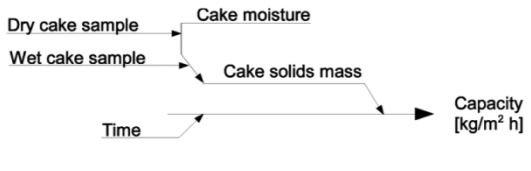
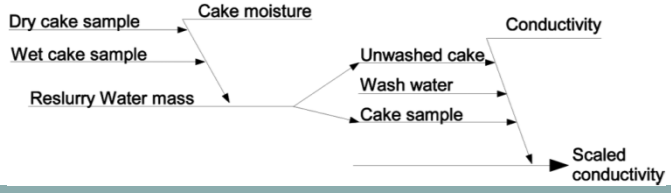
Filtration

The goal of the modelling strategy for the **cake washing** was to determine the simplest empirical models and compare these with theoretical equations complemented with linear terms.
It was found that the empirical equation could model the results more accurately than the theory-based equations could.

Huhtanen et al. 2012





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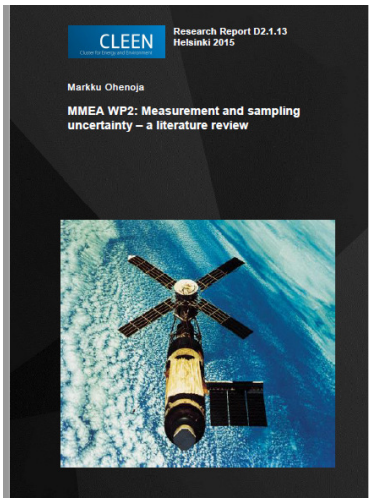
Guidance documents on measurement uncertainty



This review presents the central features of the methods related to measurement uncertainty and sampling error estimation. Also the uncertainties in digital signal processing and virtual measurements, and the alternative methods in evaluating those, are addressed.

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In the framework of the European Metrology Research Programme (EMRP) project ENV05 OCEAN (Metrology for ocean salinity and acidity)1, the dissolved oxygen concentration field (in situ) intercomparison (FieldOxy 2014) test was organized onboard R/V Aranda on April 23, 2014 in the Gulf of Finland

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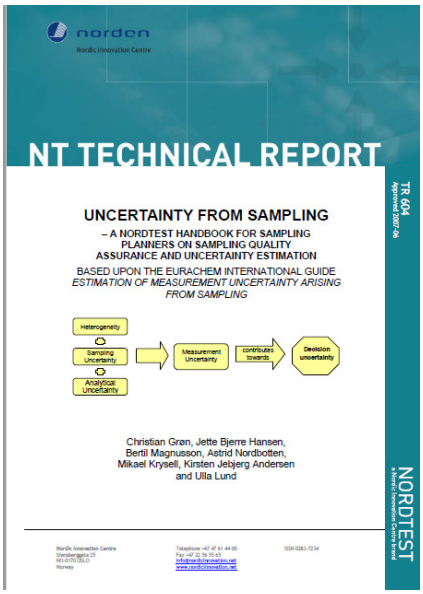

Nordic Innovation Centre project number: 04130

"The handbook is an extract of and based upon the principles, methods and text of the international Eurachem Guide Estimation of measurement uncertainty arising from sampling. The Eurachem guide is more extensive and provides details on theory and additional examples. The basic reference for the text in this handbook is the above-mentioned Eurachem guide."

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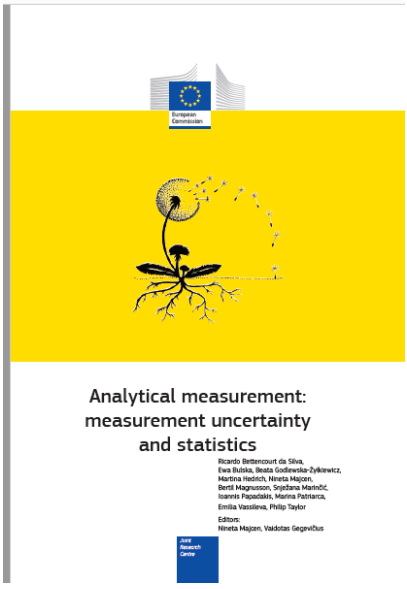

TrainMiC® programme publication

Institute for Reference Materials and Measurements
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Training in Metrology in Chemistry
European Commission

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Australian Government
Bureau of Rural Sciences
National Measurement Institute

Maintaining product integrity in the Australian seed and grain supply chain – the role of sampling and testing for GM events

Osman Mewett, Kerry R Emslie, Hilary Johnson, Jacqueline Lizzio, Kim L Dibley, E John Murby and Paul Hattersley

Report by Australian Bureau of Rural Sciences, National Measurement Institute-

Reference to the Guide through application of ISO 17025 :

"GMO testing laboratories may also choose to be certified under ISO 17025:2005 – General requirements for the competence of testing and calibration laboratories. This Standard specifies general requirements for the competence to carry out tests and/or calibrations, including sampling."

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Wide impact of Eurachem Guide on UfS

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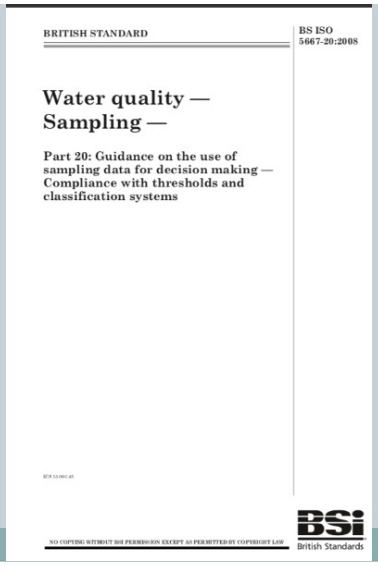

BRITISH STANDARD

BS ISO 5667-20:2008

Water quality — Sampling —

Part 20: Guidance on the use of sampling data for decision making — Compliance with thresholds and classification systems

BSI British Standards


INTERNATIONAL STANDARD

ISO 18400-104

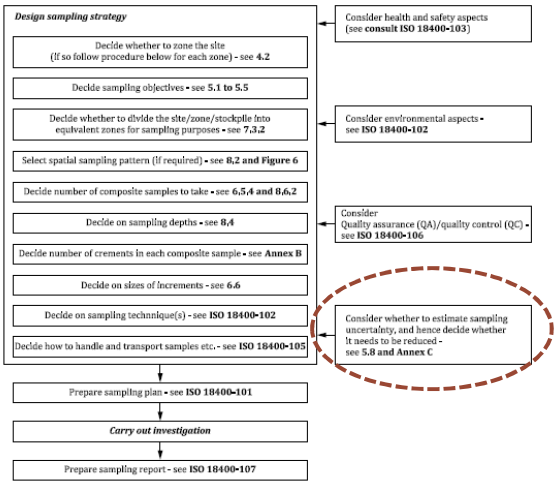
First edition 2018-10

Soil quality — Sampling —

Part 104: Strategies

Qualité du sol — Échantillonnage — Partie 104: Stratégies

ISO 18400-104:2018(E)



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Summary

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Methods of estimation of UfS have been widely applied across sectors since the 1st edition of the Guide both by metrological institutions and researchers.
- Studies by metrological institutions focus mostly on monitoring- move away from standard based and towards performance-based requirements

Criteria for selecting preferred method:

- Sampling system strongly defines selection of approach-

e.g. targets variably heterogeneous- sampling without mixing → empirical approach is preferred

- Solid matrices (soil, sediment) dominate in example case studies → historical development

EU-wide WFD for water quality has triggered research in UfS

- Emerging questions from empirical studies find answers in the new edition of the Guide (e.g. application of uncertainty factor when dealing with log-normal distributions)

Thank you

The support of this presentation by The Analytical Methods Trust Fund of the RSC in acknowledged

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