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# Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

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## Sampling contribution to measurement uncertainty

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# Sampling contribution to measurement uncertainty

## from qualitative to quantitative estimation

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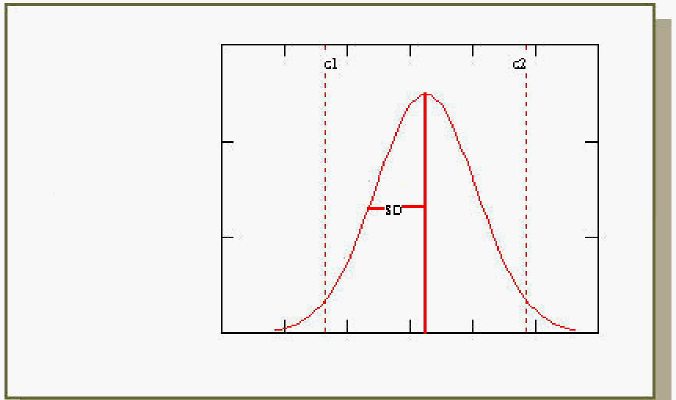
Workshop on "Understanding and Evaluating Radioanalytical Measurement Uncertainty"

ICTP, Trieste (Italy), 5-16 November 2007




**APAT - Agenzia per la protezione dell'ambiente e per i servizi tecnici**

# Contents

- Background
- Topics:
  - Measurement uncertainty and its role;
  - International requirements on sampling uncertainty;
  - Factors influencing the measurement uncertainty;
  - Sources of uncertainty qualitative comparison

# Background

- Uncertainty is the most important single parameter that describes the quality of measurements, affecting decisions based upon its value.

- Significant work has been done on how estimate the analytical uncertainty and guides/instruction on it are easily available for most field of analysis

- In the past, it has been pointed out that in environmental analysis sampling strongly influences the final analytical data and it contributes to the measurement uncertainty.

  - *A measurements almost invariably requires the action of taking a sample*

# Background

- An excess of errors due to sampling in relation to sample preparation and analysis has often been proclaimed, but endeavors to analyse and improve this situation are rare.
- Qualitative estimation have been made and in general the conclusion was :

"***Sampling impact is greater than analysis !***"

- Some researchers addressed their attention on this issue, starting from different points of view.

# What is $U_{meas}$ ?

- U of measurement is defined as:

"Parameter, associated with the results of measurement, that characterizes the dispersion of the values that could be reasonably attributed to the measurand (ISO, 1993 GUM, B.2.18)

***Formal definition***

# More informal definition

- But U of measurement is even:

"the interval around the results of the measurement that contains the *true value* with high probability"

***Informal definition***

- U is the value after ± of your measurement value

***The simplest, intuitive, but incomplete definition***

# Uncertainty is not error

- **Error**:

"the result of a measurement minus a true value of the measurand" (VIM)

The true value cannot be determined and in practice we consider a ***conventional*** true value.

The error is an idealised concept and errors cannot be known exactly

# Uncertainty is not error (2)

- You can have results very close to the value of the measurand (**negligible error**), but at the same time you can be unsure about how close is your result to the value (**significant uncertainty**)

<u>Random errors</u>

- Arise from unpredictable variation of influence quantities. It is possibile to reduce (e.g. increasing the number of measurements)

<u>Systematic errors</u>

- Part of the errors that remains constant or varies in a constant way. It cannot be reduced as it is independent by the measurement

# The role of the uncertainty

- All results have an uncertainty on their value
- It is a critical property of an analytical result, not to be considered as an option
- ISO/IEC 17025 requires that uncertainty must be evaluated

# The role of the uncertainty (2)

- The uncertainty allows to assess the reliability of any result obtained
- It is a unique tool aimed at knowing the confidence of any decisions based on its use
- The comparison between measurement results is based on uncertainty

# Sources of uncertainty

- Uncertainty may arise from different sources associated to all the measurement process
- Each source of uncertainty represents an uncertainty component that can be identified and even quantified

# Sources of uncertainty

## ICRU (2006)

- Laboratory uncertainties, e.g.
  - statistical counting variation,
  - geometrical differences in samples and containers,
  - sample weighing and moisture content effects, chemical procedure variations, and cross-contamination;
- Variations in performance of the actual field-sampling protocol;
- Natural spatial and temporal variations in the individual samples collected for analysis;
- Natural spatial variations *around* the individual samples collected for analysis

# From Combined to Expanded Uncertainty

- Combining all uncertainty components (or part of them) you obtain a total uncertainty, called **combined standard uncertainty**

and if

- …. you provide an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values attributable to the measurand you have the **expanded uncertainty** (typically multiplying the combined standard uncertainty for a coverage factor).

# Which is now the problem?

- Measurement uncertainty is usually characterised, understood and controlled (regarding to analytical components), but uncertainty associated with **sampling and samples preparation** is not yet fully considered.

# International requirements (1)

- Requirements for performance characteristics of analytical methods are increasingly defined in regulation (target uncertainty, repeatability, reproducibility, recovery across a range of concentrations, etc.)
- They will be widely used within the decision making process

**What is happening for sampling ?**

# International requirements (2)

- Quality on sampling is not addressed beyond the broad requirements that (for example)

………"*the sampling method applied shall ensure that the aggregate sample is representative for the lot that is to be controlled*". (2003/78/EC: Annex I, Section 4)

# International requirements (3)

- The trend is towards:
  - the estimation of the contribution of sampling in the measurement uncertainty;
  - the statement of acceptable levels of uncertainty associated to sampling (for different kind of samples and measurement)

- The estimation of the uncertainty including the contribution from sampling is going on to be part of international standards and rules.
  - with reference to the quality management system practices, the ISO/IEC 17025 reports the sampling as a factor to be considered in total uncertainty of measurement;
  - The European Water Framework Directive 2000/60/EC

## **Commission Decision**
## Chemical monitoring and quality of analytical results in accordance with **Directive 2000/60/EC**

- "…….. sampling and sample treatment …… follow recommendations of relevant international guidelines and/or standards, including relevant parts of EN ISO 5667 Water quality – Sampling";

- "Quality control of sampling and sample handling is considered, taking into account relevant international guidelines and/or standards and, where data are available, **uncertainty related to sample collection and transport into the total measurement uncertainty** of final monitoring results".

# Sampling Uncertainty

"The part of the measurement uncertainty attributable to the sampling"

- *IUPAC Recommendation, 2005*
- *EURACHEM/Eurolab/CITAC/Nordtest, 2007*

$$u_{\text{meas}} = \sqrt{u^2_{\text{sampling}} + u^2_{\text{analysis}}}$$

# Overview of the main factor influencing measurement uncertainty (environmental analysis)

- Planning;
- Sampling;
- Transportation;
- Storage;
- Sample preparation;
- Sample pre-treatment;
- Analysis;
- Data evaluation.

# Planning

| PROCEDURE-STEP | MAIN SOURCE OF UNCERTAINTY | QUALITATIVE ESTIMATION |
|---|---|---|
| Definition of the area | Spatial variability;<br>Heterogeneity | High |
| Sampling methods | Statistical representativeness<br>contamination, loss | High, partly controllable |
| Number of samples | Statistical representativeness | High |
| Sample size (mass, volume) | Statistical representativeness | Normally low |
| Timing | Temporal variability, trends | High |

# Sampling – transportation - storage

| PROCEDURE-STEP | MAIN SOURCE OF UNCERTAINTY | QUALITATIVE ESTIMATION |
|---|---|---|
| Weather condition | Unreproducible deposition, leaching, matrix effects | Very high |
| Packaging and sample conservation during sampling | Contamination or loss by tools and container material – Losses by metabolism, volatilisation (most serious for air filter, water and animal tissue) | Controllable Moderate |
| Transportation | Contamination or loss by volatilisation, metabolism (most serious for soil and water) | High |
| Short-term long-term storage | Contamination or loss, metabolism, alteration of binding form | High / Very high |

# Sample preparation

| PROCEDURE-STEP | MAIN SOURCE OF UNCERTAINTY | QUALITATIVE ESTIMATION |
|---|---|---|
| Cleaning, washing | Contamination or loss by leaching | High |
| Drying | Loss, contamination | Moderate |
| Homogenisation | Contamination, disregard of skewed distribution | High |
| Sub-sampling | Particle and analyte distribution and heterogeneity | Moderate/High |

# Sample pre-treatment

| PROCEDURE-STEP | MAIN SOURCE OF UNCERTAINTY | QUALITATIVE ESTIMATION |
| --- | --- | --- |
| ■ Digestion<br>■ Extraction<br>■ Separation<br>■ Concentration<br>■ Matrix modification | ■ Contamination by reagents or container material, loss by adsorption, precipitation, or co-precipitation, matrix un-dissolution | ■ Controllable |

# Analysis

| PROCEDURE-STEP | MAIN SOURCE OF UNCERTAINTY | QUALITATIVE ESTIMATION |
|---|---|---|
| Injection | Inaccurate or badly adjusted tools | Moderate |
| Calibration | Physical and chemical interferences | Moderate |
| Detection | Spectral interferences | Low |
| Peak identification | automatic evaluation | Low |
| Quantification | baseline drift | Low |

# Data evaluation

| PROCEDURE-STEP | MAIN SOURCE OF UNCERTAINTY | QUALITATIVE ESTIMATION |
|---|---|---|
| Averaging | Disregard asymmetric distribution | Moderate |
| Confidence of interval | Disregard asymmetric distribution | Moderate |
| Trend detection | Disregard of natural variability and fluctuation | High |

# GUM foresees:

- specification of the measurand;
- identification of the uncertainty sources;
- quantification of the uncertainty components;
- calculation of the combined uncertainty.

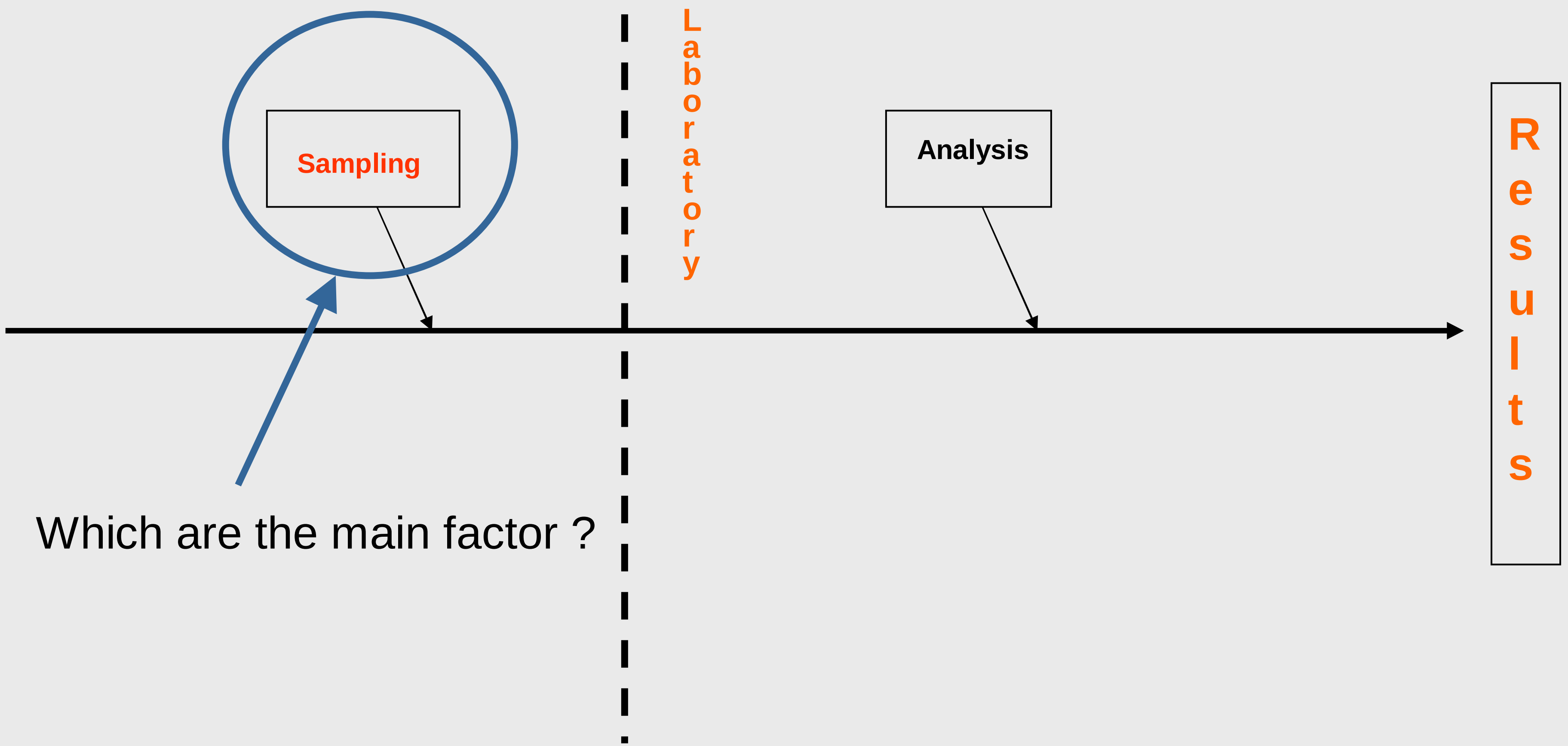
# Uncertainty sources identification

Cause-effect diagram

**(so-called Ishikawa or fish-bone)**

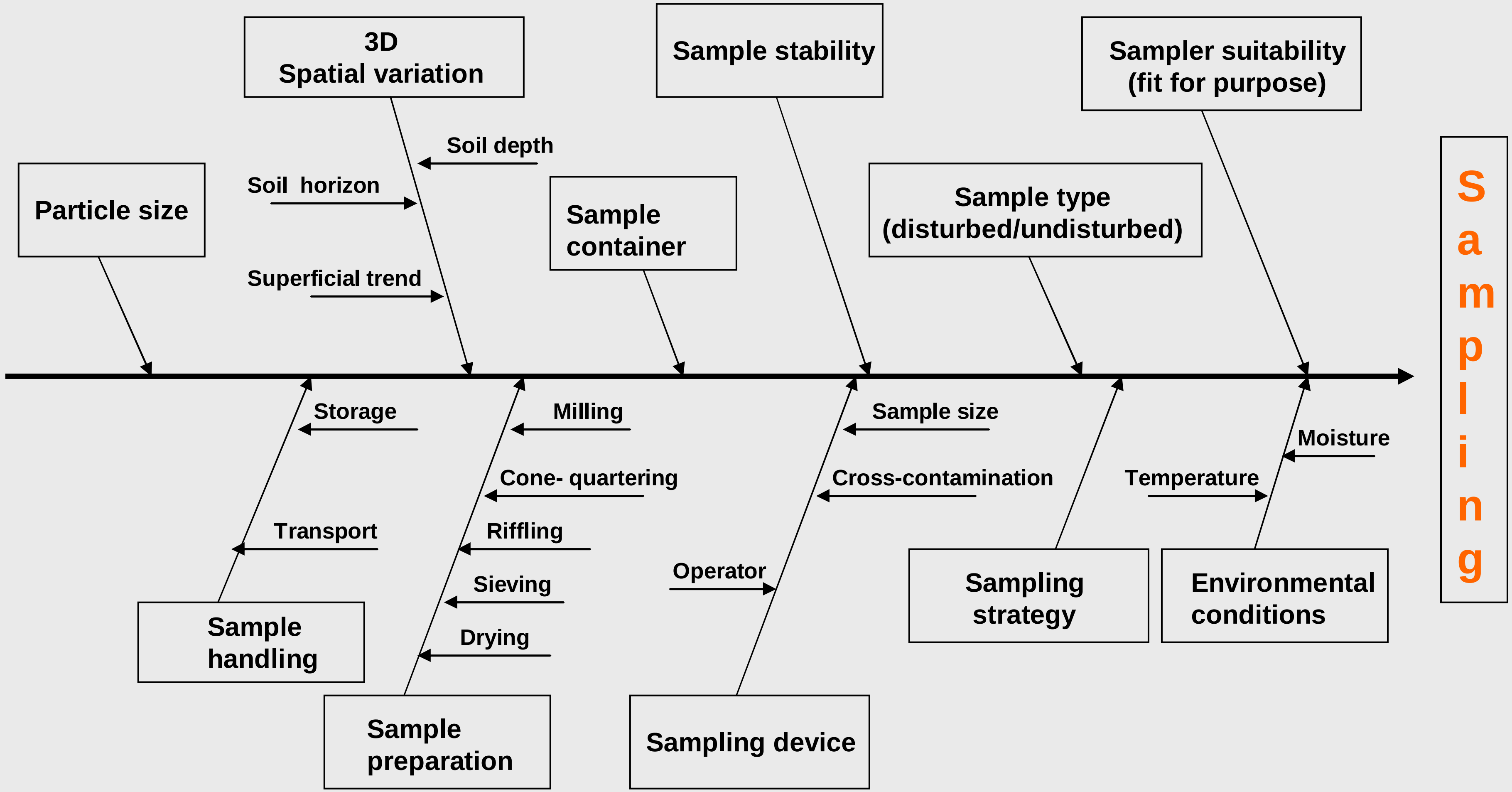
- shows the parameters considered and
- how they relate to each other
- avoids over-counting

# Uncertainty sources identification




Which are the main factor ?

# Soil sampling cause-effect diagram



# Cause-effect diagram

Depending on the experimental design some uncertainty components may be:

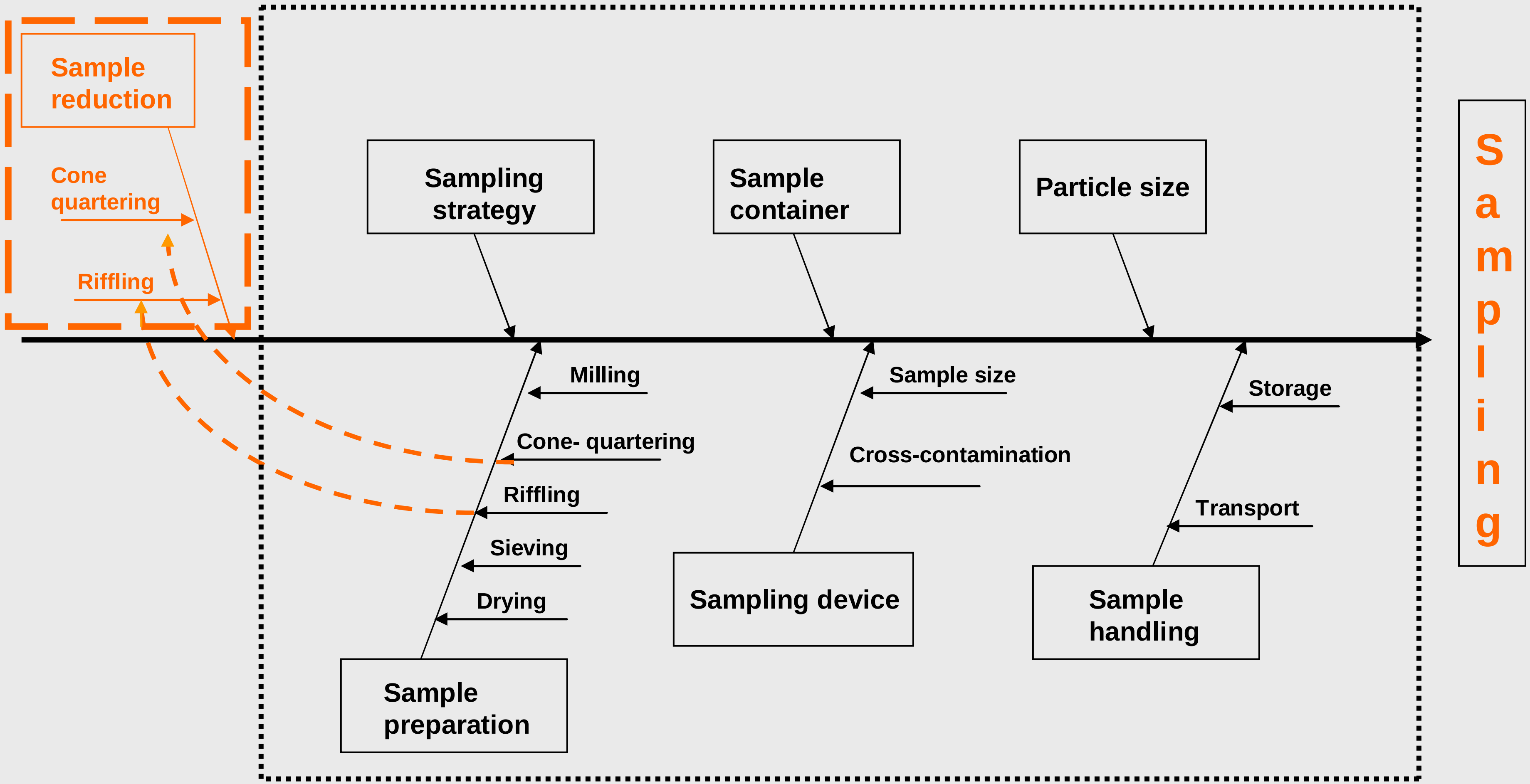
- ruled out (operator, environmental condition)
- not relevant (spatial variation, sample type, sample stability)

# Cause-effect diagram

The soil sampling uncertainty components, once identified, can be considered (if convenient) as "blocks"

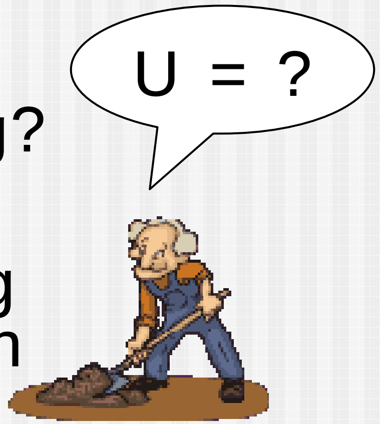
- aggregating some components (particle size, sampling device, sampling strategy, sample handling, sample container, sample preparation)
- separating some sample preparation components (sample reduction)

# Aggregated cause-effect diagram



# Quantitative estimation

- Qualitative estimates have been made.
- But how may I have a reliable estimates of uncertainty from sampling?




- Some researchers/institutions, starting from different point of view, worked on this issue.

- P. Gy, (France);
- A. Desaules, (Swiss);
- U. Kuerfurst, (Germany)
- M. Ramsey and M. Thompson, (Great Britain);
- APAT (Italy).

# Conclusion

- Measurement uncertainty must include sampling uncertainty as it is part of the measurement process
- Each source of uncertainty may have a different impact
- A clear identification of the possible contributions allows a better understanding of the overall uncertainty
- The estimate of sampling uncertainty is a parameter of the quality of sampling