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Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

5 - 16 November 2007

Sampling and Uncertainty

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Sampling & Uncertainty

Paolo de Zorzi, Sabrina Barbizzi

Workshop on "Understanding and Evaluating Radioanalytical Measurement Uncertainty"

ICTP, Trieste (Italy) 5-16 November 2007

The “menu” of the day

- Sampling in the measurement process
  (P. de Zorzi)
- Sampling contribution to the measurement uncertainty: from qualitative to quantitative estimation
  (P. de Zorzi)
- An outline of the methods for the estimation of uncertainty including the contribution from sampling
  (S. Barbizzi)
- Estimation of uncertainty arising from sampling by using variogram parameters
  (P. de Zorzi)
- Exercises

Sampling in the measurement process

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- AIM
- BACKGROUND
- TOPICS:
  - Terminology
  - Sampling and measurement process
  - Sampling plan
  - Sampling strategy and pattern
  - Types of sample
  - Sample preparation

Aim

- Are we speaking the same language ?
- Why do you sample ?
- When do the sampling start and end ?
- Which are the key-elements of sampling process ?

Background (1)

- First scientific approach to sampling was developed in the **20's** mainly addressed to useful pattern for solution of general agricultural problem;
- From the **50's** theories on sampling was developed for the mining field.
- Sampling guides and literature were published in order to define a common framework for different field;
- In the **recent past** studies on different sampling issues (sample preparation, uncertainty, intercomparison) were developed.

Background (2)

- Most attention has been focused in the past on analytical procedures/techniques and laboratories aimed at improving the quality of the measurements

BUT

- Variability from this sources may be small in comparison with the inherent variability arising from sampling

An analytical result cannot be better than the sample on which it was performed.

Background (3)

- Sampling has been frequently overlooked and considered out of the measurement process.
  - If you have a “correct” standard sampling protocol your sample will be representative and correct;
  - You need well trained operator to carry out the sampling protocol.
  - The measurements is only in the laboratory

Background (4)

- Sampling is not a stand-alone operation; it is part of a chain of measurement.
  - In-situ measurements (i.e. portable XRF) is a typical example
  - placing the instrument/sensor on the ground, you are measuring and, at the same time, you are taking a sample

⇓

Sampling is included in measurements process

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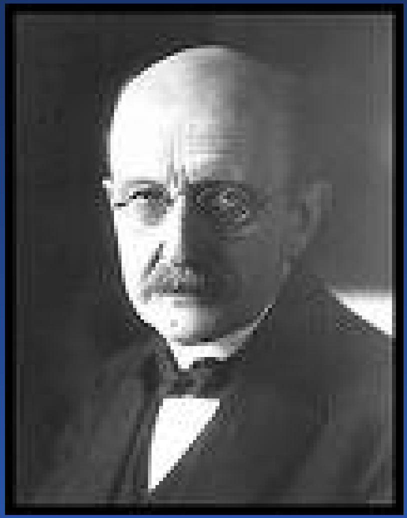
Terminology



Are you a poet ?

Maybe YES, but now you have to be a scientist/technician

- It is not acceptable ambiguity in the scientific/technical terms used.
- Effort has been made in order to overcome confusion, ambiguity and contradiction in the usage of terms and clarification of their definitions in the field of sampling

Terminology (2)

General

1. IUPAC Recommendation 1990 “Nomenclature for sampling in analytical chemistry”
2. ISO 3534-1: 1993. “Statistics-Vocabulary Part1: Probability and general statistical terms”
3. ICRU 2006, “Sampling for Radionuclides in the Environment”, (Chapter Glossary)

Water / Sediment

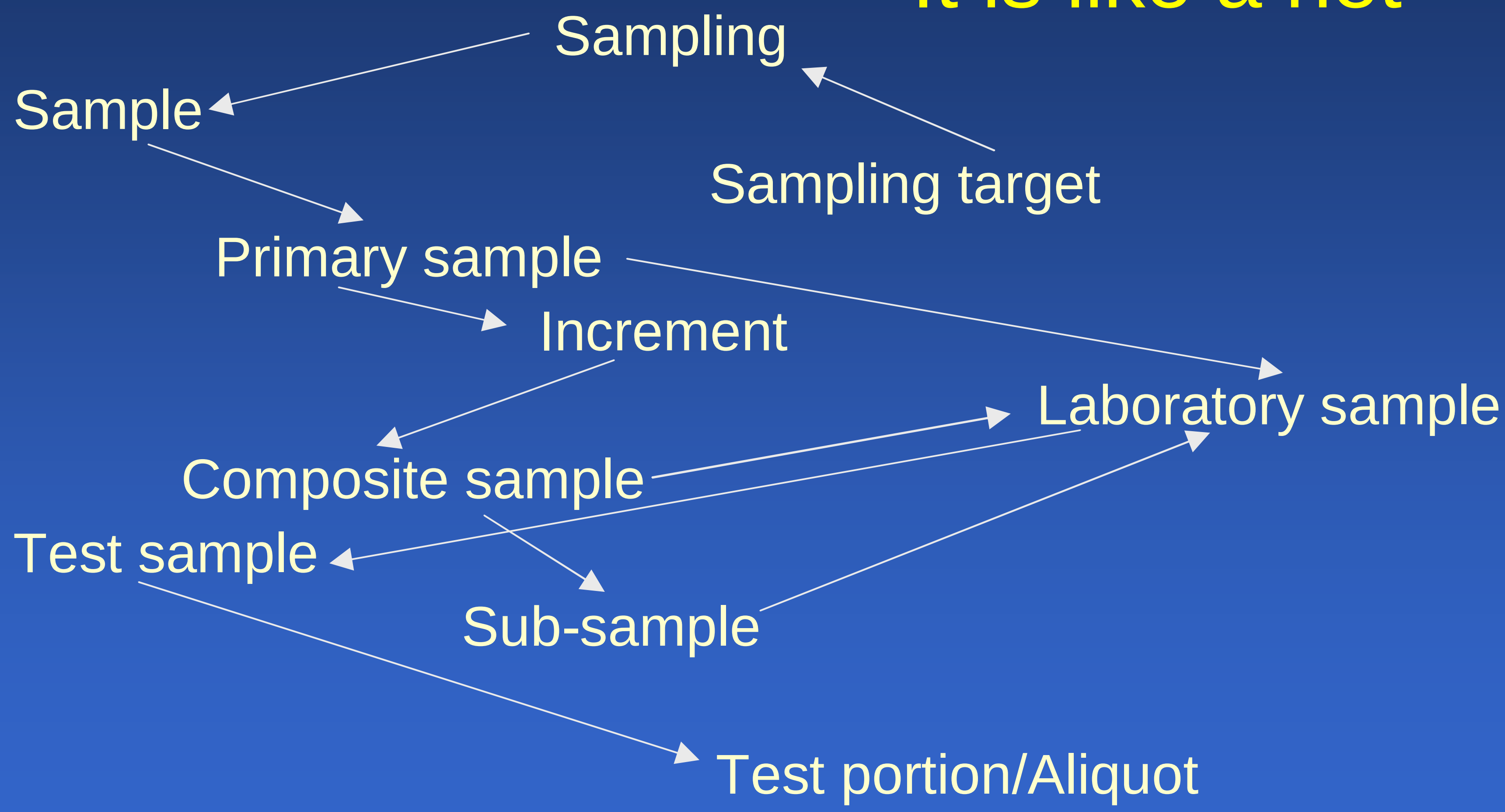
1. ISO 6107-2 “Water quality-Vocabulary-Part 2”
2. ASTM D1129-95 “Terminology relating to water”
3. ASTM D 4410-97 “Terminology of fluvial sediment”

Soil

1. IUPAC Recommendation 2005 “Terminology in soil sampling”
2. ISO 11074-2:1998 “Soil Quality-Vocabulary-Part 2: Terms and definitions relating to sampling”
3. ASTM D653-96 “Terminology to soil, rock and contained fluids”

Terminology (3)

It is like a net



Terminology (4) Soil

- Sampling = Process of obtaining a sample
  IUPAC (2005)

- Sampling = Process of drawing or constituting sample

  ISO 3534-1 (1993)

- Sample = A portion of material selected from a larger quantity of material

  ISO 11074-2 (1998)
  IUPAC (1990)
  IUPAC (2005)

Terminology (5)

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

1) A river transect

2) 1000 m^2 of arable land

3) a lettuce bay

……………………

n) 5000 m^3 of compost

Terminology (6) Water/sediment

Definition 1

- Sampling = process of removing a portion, intended to be representative, of a body of water for the purpose of examination of various defined characteristics
  ISO 6107-1
  ISO 3534-1 (1993)

Definition 2

- Sampling = Obtaining a representative portion of the material concerned
  ASTM D 1129-95

- Sample = portion, ideally representative, removed from a specified body of water, either discretely or continuously, for the purpose of examination of various defined characteristics
  ISO 6107-1

Terminology (7)

In conclusion:

- When you are speaking or writing about sampling and any other related concept, use the appropriate words as stated by rules and/or international guides.

You will minimise misunderstaing

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Measurement & Sampling process

- Whenever you are requested to characterize the property of an object of interest you have to sample it

but......

  - - which is the sampling “domain” ?
  - - which is your final objective ?
  - - which is the property to be measured ?
  - - which analytical method will be used or are available?
  - - how the measurements results will be managed ?

Measurement & Sampling process

Process step	Form of material	Description of process step
Sampling	Sampling Target	Collection of a single sample, or several increments combined into composite sample
Physical sample preparation	Primary Sample	Comminution and/or splitting
	Sub-sample	Further comminution and/or splitting
	Laboratory sample	Physical preparation, e.g. drying, sieving, milling, splitting, homogenisation
	Test sample	Selection of test portion for chemical treatment preceding chemical analysis
Analysis	**Test portion**	Chemical treatment leading to analytical determination
	Test solution	Determination of analyte concentration

M H Ramsey and S L R Ellison (eds.)

Eurachem/EUROLAB/ CITAC/Nordtest/AMC Guide: ***Measurement uncertainty arising from sampling: a guide to methods and approaches Eurachem*** **(2007)**

Measurement & Sampling process

- Sampling, following a sampling plan, starts from the identification of the sampling target and ends ordinarily after preatrement steps, with the removal of the test portion/aliquot from the test sample

- In some cases, sampling relates to the selection of locations for the purpose of in-situ testing carried out in the field without removal of material (solid, liquid, etc.)

Measurement & Sampling process

Analysis

Result

Measurement & Sampling process

Parties involved:

- The customers (public institution, universities, citizens, etc.);
- The responsible of the measurement;
- The responsible of sampling planning;
- The sampler;
- The analyst;
- The decision maker

Measurement & Sampling process

The measurement process needs all parties involved interact one to each other

The quality of the measurements and, therefore the quality of the decision, depends on the a continuous flux of information among the parties

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Sampling plan

Sampling needs to be planned in order to be able to say at the end of the overall measurement process, with a known uncertainty, and under stated condition:

1. How much contaminated is a field;
2. Which is the activity density of ^{137}Cs in a forest;
3. How much Arsenic is in a fish tissue;
4. Is the quantitative limit (threshold value) exceeded?
5. ......
6. ....

The sampling plan must reflect our purposes/objectives

Sampling Plan

A sampling plan define the general and the specific objectives of measurement process and how these objectives can be practically reached.

A general scheme can be the following

1. Objective
2. Preliminary information
3. Strategy/Pattern
4. Sampling operation
5. Safety
6. Sampling report

General objectives

1. Researches, studies to determine the general quality of the environmental matrix of interest
2. Sampling aimed at preparing maps describing spatial distribution (i.e. radionuclide soil maps)
3. Environmental control to support legal or regulatory action
4. Environmental monitoring
5. Sampling as part of a hazard or risk assessment
6. Validation studies

Objectives must be precisely defined in order to assess cost and quality control

Specific objectives

- Nature, concentration and distribution (in space and/or time) both of naturally occurred substances and contaminants
- Presence and distribution of biological species
- ....

Specific objectives should define the data quality requirements (known meas uncertainty, LOQ, etc.) and confidence level acceptability

The specific objectives drive to a suitable sampling

Preliminary information

Whatever the sampling objective a preliminary survey of the sampling target is recommended (more difficult in emergency situation)

1. Desk-top study
   - Hystorycal information (i.e. previous investigation, sampling target use, etc.)

2. Site visit
   - Information on the access to the sampling target;
   - Specific limitation and or risks
   - Presence of infrastructure

Strategy

Decision must be taken regarding the sampling strategy

1. Patterns
2. Sampling location/point
3. Depth (both for water and soil)
4. Type of samples to be collected
5. Sampling techniques

Sampling operation

1. Sampling devices
2. Sampler (personnel)
3. Storage condition to be assured
4. Preservation
5. Labeling and transportation

The sampling activity should be carried out in connection with the analysts

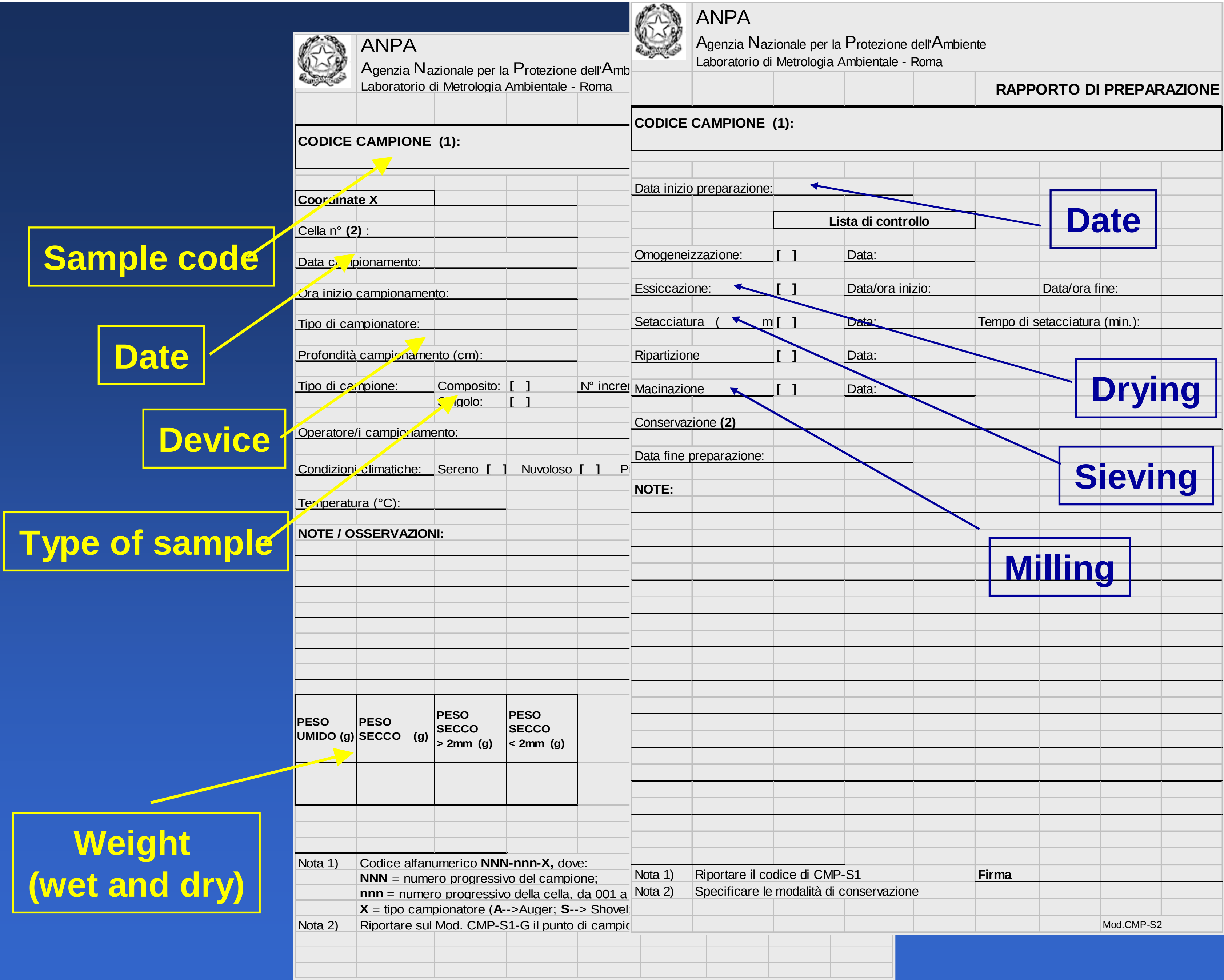
Safety

On the basis of the information available (site survey and sampling objective) some elements should be considered:

1. The material to be sampled (harmful substances of a contaminated soil, bottom sediment, powder material, etc);
2. The sampling location (presence of vehicles or infrastructure, the ground surface, the river condition, etc.);
3. The sampling situation (i.e. climate condition)
4. Precaution in the sampling operation due to the type of sampling device or to the use of some chemical substances as preservatives

Sampling report

- A **sampling report** including all the relevant information related to the sampling operation should be prepared.
- The report is based on the information acquired before and during the sampling
- A **sampling form** structured with “blank-field” to be filled during the operation should be linked to each sample collected



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Laboratorio di Metrologia Ambientale - Roma

CODICE CAMPIONE (1):

Coordinate X
Cella n° **(2)** :
Data campionamento:
Ora inizio campionamento:
Tipo di campionatore:
Profondità campionamento (cm):
Tipo di campione: Composito: [ ] N° incre
Singolo: [ ]
Operatore/i campionamento:
Condizioni climatiche: Sereno [ ] Nuvoloso [ ] P
Temperatura (°C):
NOTE / OSSERVAZIONI:

PESO UMIDO (g)	PESO SECCO (g)	PESO SECCO > 2mm (g)	PESO SECCO < 2mm (g)

Nota 1) Codice alfanumerico **NNN-nnn-X,** dove:
NNN = numero progressivo del campione;
nnn = numero progressivo della cella, da 001 a
X = tipo campionatore (**A**-->Auger; **S**--> Shovel
Nota 2) Riportare sul Mod. CMP-S1-G il punto di campio

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RAPPORTO DI PREPARAZIONE

CODICE CAMPIONE (1):

Data inizio preparazione:

Lista di controllo

Omogeneizzazione: [ ] Data:
Essiccazione: [ ] Data/ora inizio: Data/ora fine:
Setacciatura (m [ ] Data: Tempo di setacciatura (min.):
Ripartizione [ ] Data:
Macinazione [ ] Data:
Conservazione **(2)**
Data fine preparazione:
NOTE:

Nota 1) Riportare il codice di CMP-S1 **Firma**
Nota 2) Specificare le modalità di conservazione

Mod.CMP-S2

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Sampling Strategy/Pattern

Different sampling strategies are suitable for different objectives

1. Judgmental sampling
2. (Simple) random sampling
3. Stratified (random) sampling
4. Systematic sampling
5. Non systematic sampling

Judgmental Sampling

It is designed by the subjective knowledge and judgment of experts

For example:

- Sampling within a specific area of a contaminated site aimed at the determination of distribution of some radionuclide.

1. You know well the plants, the infrastructure and the possible pathway
2. You have information about previous environmental investigation on the same area
3. You know, for example, the precise point of discharge probably associated to the measurand of interest

Judgmental Sampling (2)

Advantage:

- Fastly designed and carried out;
- The data might allow estimates of the maximum exposure to the contaminants.

Disadvantage:

- High risks of sample biased if based on wrong information
- It does not allow statistical analysis.

Random Sampling

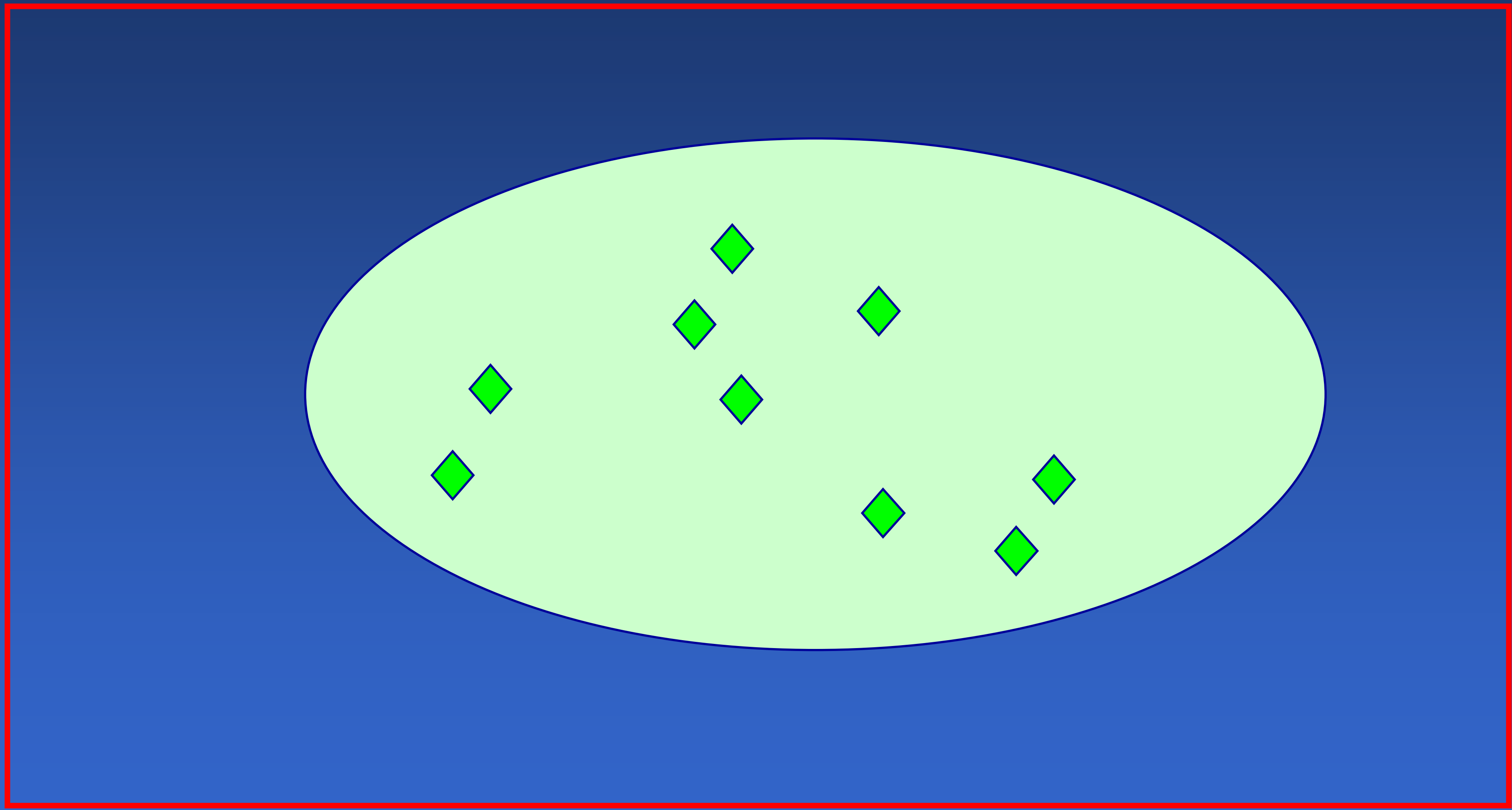
The selection of the sampling points is arbitrary and independent by the location of other sampling points

For example:

- Determination of the "gravel content" within a an arable land.

1. You assume the property to be determined was homogeneous within the sampling targets;
2. From a statistical point of view every sampling unit in the population has an equal probability of being included in the sample

Random Sampling (2)



Random Sampling (3)

Advantage:

- Unbiased sample
- Possible statistical interpretation

Disadvantage:

- Poor efficiency in case of difficulties in randomization
- Limited to very homogeneous population for the property of interest.

Stratified (Random) Sampling

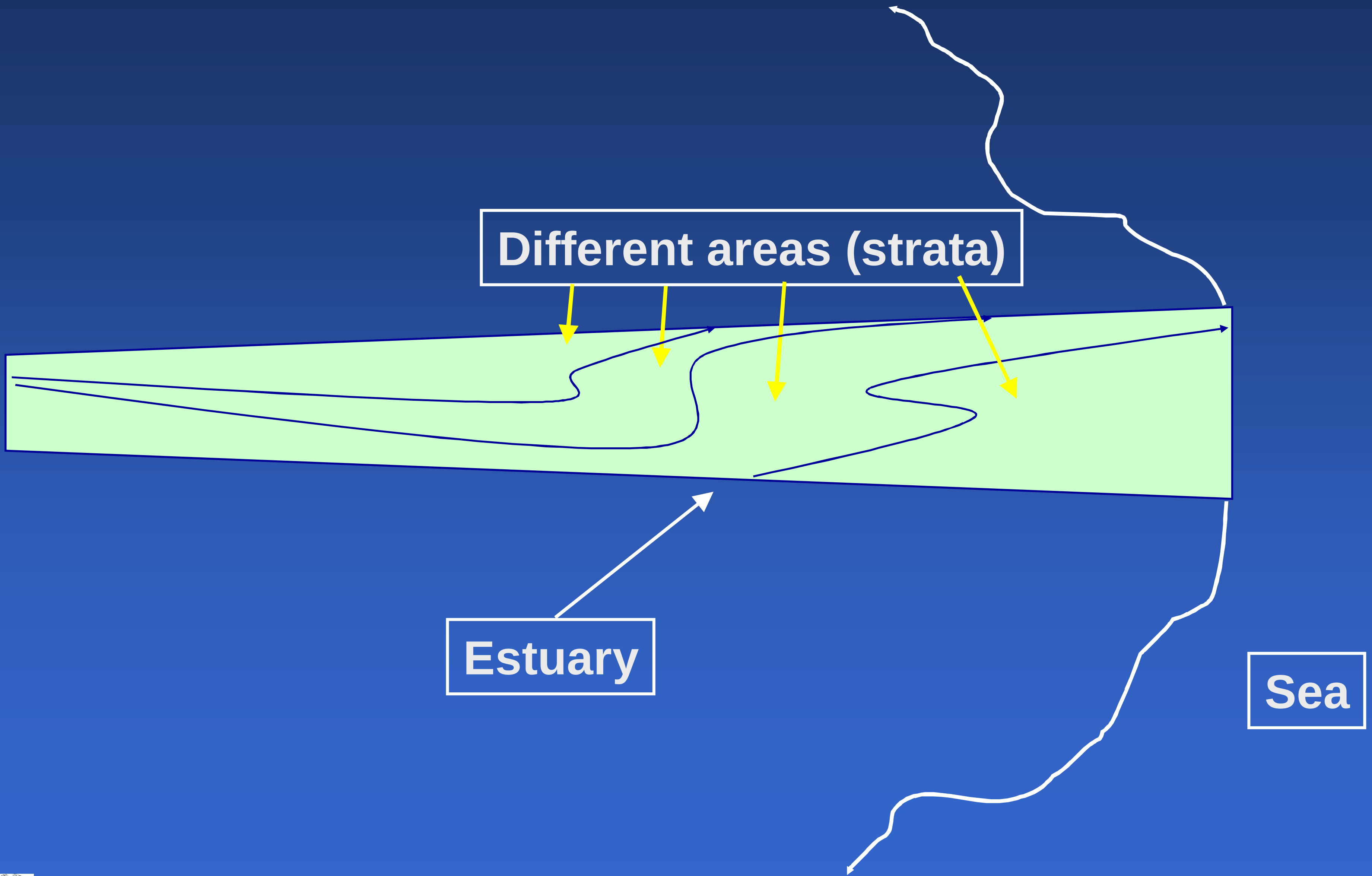
The selection of the sampling points is based on the previous sub-division of the sampling target into smaller areas called strata

For example:

- Determination of ^{137}Cs activity density into sediments of an estuary.

1. You know that sediment particle size distribution is not homogeneous
2. You know the distribution of the different type of sediment within the estuary
3. You can sub-divide the sampling target into smaller areas, each of which is more homogeneous than the entire population to be sampled

Stratified (Random) Sampling (2)



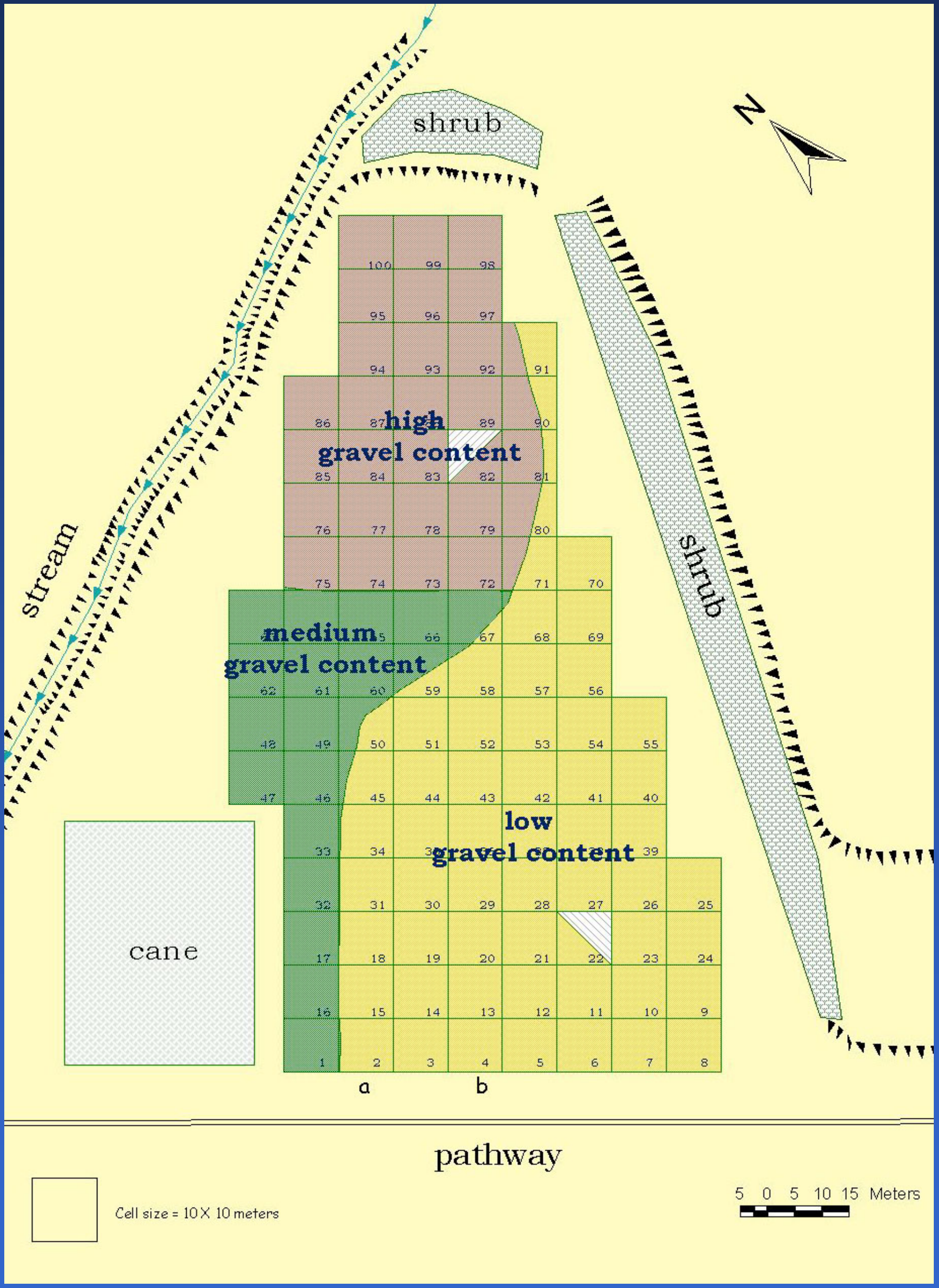
Stratified (Random) Sampling (3)

Qualitative evaluation of the soil fraction with size above 2 mm

- brown area: high gravel content

- green area: medium gravel content

- yellow area: low gravel content



Stratified Random Sampling (4)

Advantage:

- More representative samples
- More precise estimation than simple random.
- Possible statistical interpretation

Disadvantage:

- More information requested *a-priori* for performing the stratification
- Costly approach if detailed information are not available
- Risk of biased results if wrong stratification is done.

Systematic Sampling

The selection of the sampling points is done by some logical and organized methods

For example:

- Determination Cr mass fractions into the soil of a possible contaminated site.

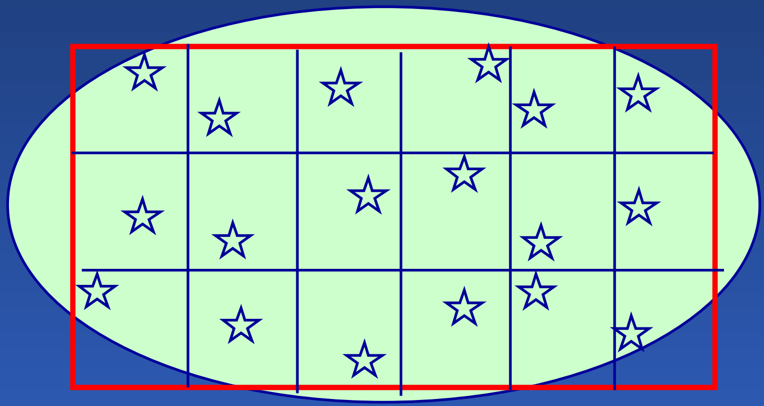
1. You don't know the distribution of the element
2. Possible presence of "hot-spots"
3. No information about the source of contamination

Systematic Sampling (2)

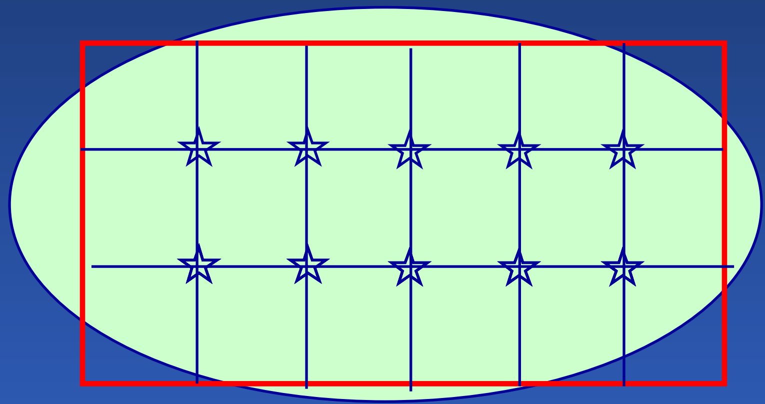
- Grid or triangular (sampling from the nodes);
- Transect;
- Grid (sampling within the cells).

- Sampling within the cells you can select the sampling points at the center or by randomization. In the first case the design remains **Systematic,** in the latter case you are following a **Systematic Random Sampling**

Systematic Sampling (3)



Systematic random sampling



Systematic (grid) sampling

Systematic Sampling (4)

Advantage:

- Easily designed and implemented in practice
- Easily varied (dimension of the grids)
- Unbiased as long as the starting point is selected randomly
- Interpolation between the sampling points for a better evaluation of pattern.
- More representatives than random sampling
- Suitable in most of the cases of environmental monitoring

Disadvantage:

- High number of samples (less in case of transects)
- Costly approach, if singles samples are analysed
- Risk of biased results in the case of variation due to periodicity of the measurand.

Non-Systematic Sampling

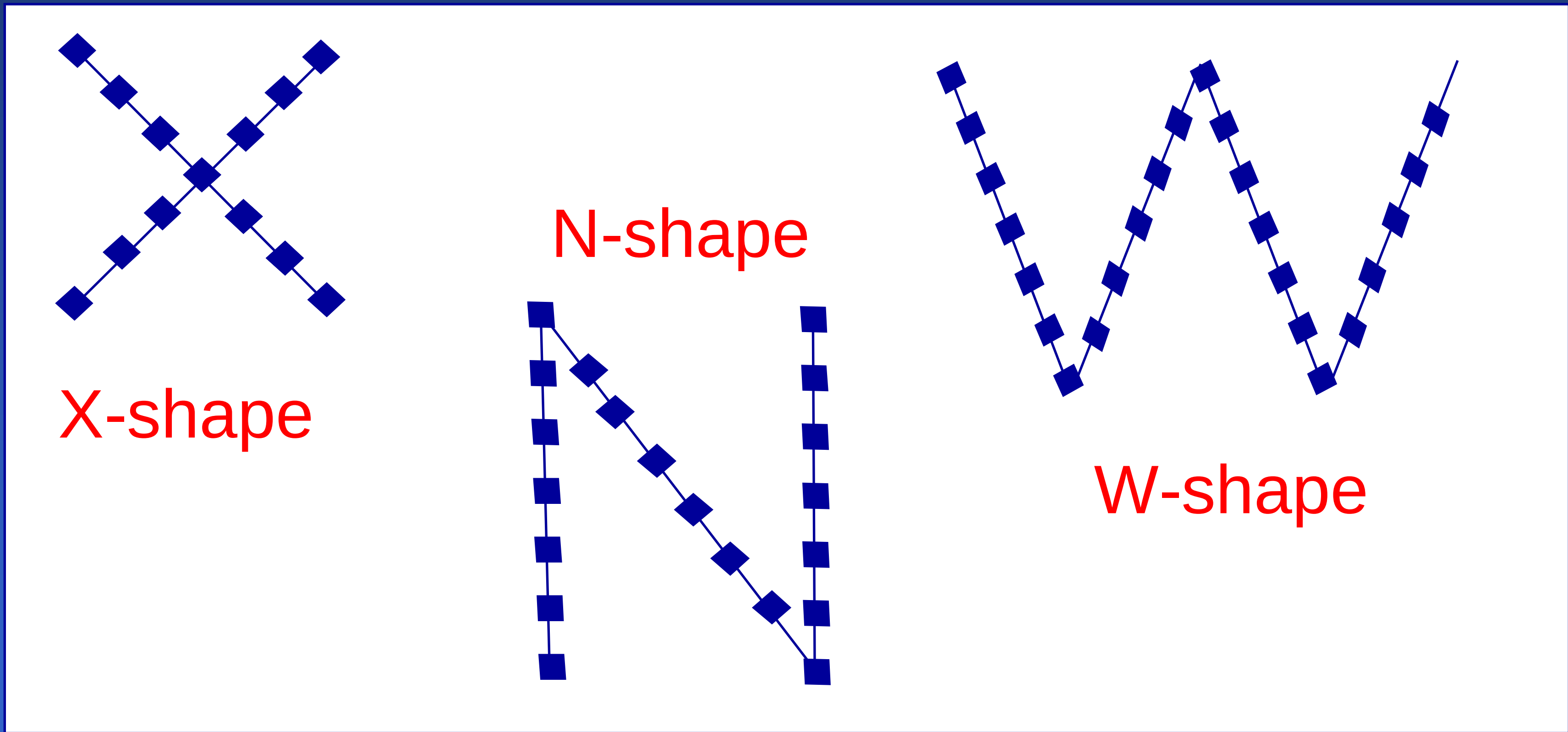
The selection of the sampling points is done following irregular designs

For example:

- Determination of some fertility properties in an agricultural field.

1. You assume the homogeneity of the sampling target
2. Low budget available

Non-Systematic Sampling (2)



Irregular patterns

Non-Systematic Sampling (3)

Advantage:

- Easily designed and implemented in practice
- Easily varied

Disadvantage:

- Limited to few cases and matrices (only uniformly distributed areas)
- In soil sampling does not reveals high level of point contamination
- Risk of biased results in the case of some irregular pattern (i.e. X-shape).

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Type of sample

- Each measurements process (including sampling), on the basis of a stated sampling strategy, is characterized by the constitution of different types of sample

- Related terms and typology reflect the stage of the sampling process

Type of sample (1)

The main classes to be considered are:

- Primary sample – Increment - Single sample
- Composite sample
- Sub-sample
- Laboratory sample
- Test sample

Test portion / Aliquot

Primary sample

The collection of one or more increments or units initially taken from a population

- It refers to the fact that the sample is taken at the first stage of the sampling
- Pooling more increments you obtain a **composite sample**

Primary sample

Composite sample

The collection of more increments/sub-samples mixed together in appropriate portions, either discretely or continuously, from which the average value of a desired characteristic may be obtained

- Composite sample might be both of large and small size (it depends on the increments)
- Useful when you don’t need detailed information about the distribution of the property (in space and time)
- It reduces the analytical costs
- It is normally splitted and/or comminuted to obtain **sub-sample**

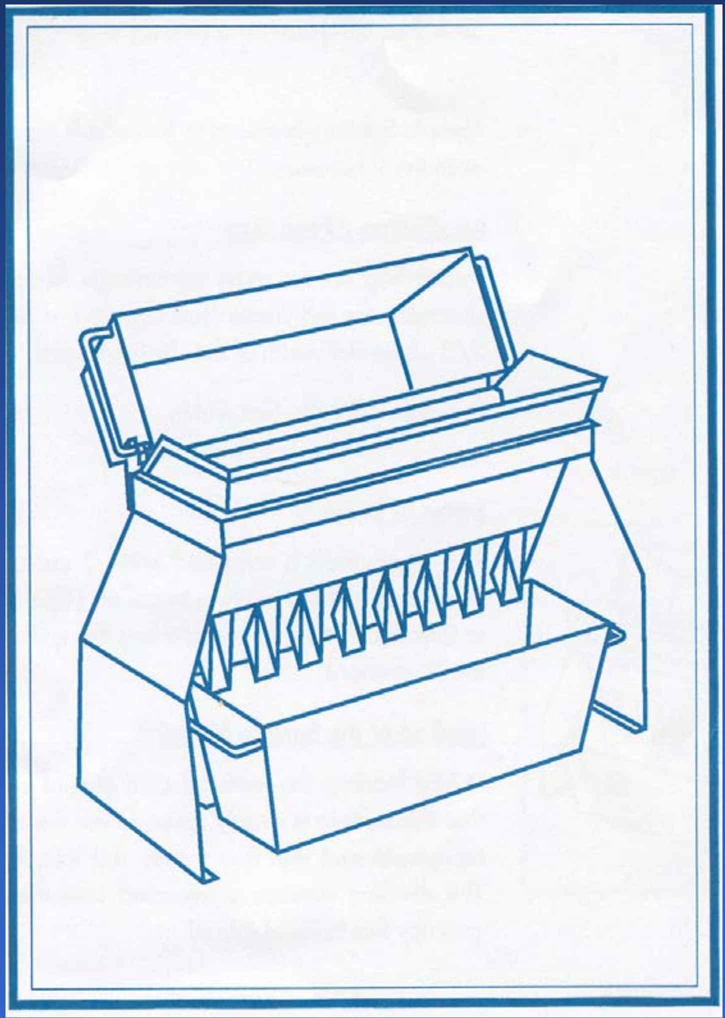
Sub-sample

A sample taken from a sample of a population

It may be selected:

- by the same method as was used for selecting the primary sample or
- by using appropriate devices aimed at reduce the sample size (weight, volume, etc.)

Sub-sample



Laboratory sample

Sample as prepared for sending to the laboratory and intended for inspection or testing

- It may be directly a primary sample or the result of the different sample preparation steps from a primary sample
- Typical laboratory samples are:
  - 1 L groundwater bottle potentially contaminated by PCBs;
  - 500 g of contaminated soil by trace elements;
  - 1 kg of vegetation harvested containing unknown activity concentration of radionuclides
  - ……………………………….

Laboratory sample (2)

- Sampling continues in the lab by physical preparation of the laboratory sample to obtain a test sample
- Typical physical preparation activities might be:
  - Drying (solid matrices);
  - Sieving (solid);
  - Filtering (liquid); → Sub-sampling
  - Grinding and milling (solid)

Test sample

Sample prepared from the laboratory sample, from which the test portion are removed for testing or analysis

- The test sample represent the last stage of the sampling, even if it is carried out **WITHIN** the laboratory
- It is the “object of the desire” for the analyst, not interested on sampling !

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Sample preparation

The set of material operations (such as reduction of sizes, mixing, dividing, etc.) that may be necessary to transform a sample into a laboratory or test sample

- This step may occur both in the field and in the laboratory
- The sample preparation should not, as far as possible, modify the ability of the sample to represent the population from which it was taken

Sample preparation (2)

Some sample preparation activity:

For example: Soil/particulate matter:

- Cone and quartering
- Drying;
- Sieving
- Milling
- Splitting
- Homogenisation

Some of these activities may be performed in different order and hierarchy

Sample preparation (3)

Your laboratory sample is of about 5 kg and the test portion to be analyzed by INAA have to be at most of about 200 mg:

- During a chess game, you at first should have to decide which final of the game you want and then which should be the best “overture” for that purpose: you have to start from the end to solve your problem

Sample preparation (4)

Some possible questions

- **Question 1** : which is the particle size suitable for the test portion ?
- **Question 2** : Should I reduce the particle size (comminution) of the laboratory sample ?
- **Question 3**: Should I reduce the size (mass, volume) of the laboratory sample before possible milling ?
- **Question 4**: Which equipment is suitable for this purpose, considering the analytical objective ?
- **Question 5**: Do I need to duplicate the sample before taking the test portions ?

Sample preparation (5)

- **Question 1** : which is the particle size suitable for the test portion ?

As you need to take a very small test portions, the particle size should guarantee the lowest heterogeneity. The higher the particle size the higher the heterogeneity of the sample. Moreover it depends on the measurand (are these linked to fine particles ?) The particle size must be checked before the test portions is taken

- **Question 2** : Should I reduce the particle size (comminution) of the laboratory sample ?

Certainly yes. Commonly in the environment the particle size of the soil is higher than centimeters (stones, aggregate, etc.). You might sieve and then reduce the particle size by planetary ball mill, crush mill or other suitable equipments, each of whose have some operative limitation (i.e. max volume capacity)

Sample preparation (4)

- **Question 3**: Should I reduce the size (mass, volume) of the laboratory sample before possible milling ?

  Managing 5 kg is not easy in the lab. You have to reduce the laboratory sample up to 100-200 g. This size is more suitable for temporary storage, for subsequent operation and may fit the requirements of some equipment

- **Question 4**: Which equipment is suitable for this purpose, considering the analytical objective ?

  The equipment must be select taking into account the characteristic of the material and the analyte to determine (i.e. in milling operations agata is preferred when the analytes of interest are the metals, avoiding cross-contamination)

Sample preparation (5)

- **Question 5**: Do I need to duplicate the sample before taking the test portions ?

Depending on the type of the analyses or under legislative constraints a duplicate sample may be requested. The replicate (duplicate) must be stored in suitable condition in order to avoid short or long-range deterioration.

Summary

- The communication between technicians/scientist requires a well defined terminology, even in sampling
- Sampling is a fundamental part of the measurement process, including a wide set of operations and decisions, and it influences the quality of the final analytical results
- Sampling starts in the field and ends in the laboratory
- You have to know how much your sample is “good”

Summary

- Analysts must operate in connection with the responsible for sampling. All the parties involved are requested to interact
- Clear objectives and related strategy, together with other operational aspects, must be previously stated as part of a sampling plan
- Sampling strategy depends on the objectives
- Sample preparation is part of the sampling process and affect the quality of the final result

Where to obtain more information

- Next Lectures on the role of sampling in uncertainty estimation
- Several ISO Guides on Sampling for different matrices (general and not detailed)
- Journal of the ICRU, (2006) Report 75 “Sampling for Radionuclide in the Environment”
- IAEA-TECDOC-1415 (2004), Soil Sampling for environmental contaminants