The Abdus Salam
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International Atomic Energy Agency

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Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

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ALMERA 2005 Soil Sampling Intercomparison exercise (IAEA/SIE/01) + DVD Presentation

Paolo de ZORZI

APAT - Agenzia per la Protezione dell'Ambiente e per Servizi Tecnici
Servizio Laboratorio Metrologia Ambientale
Via Castel Romano 100
00128 Roma
ITALY

ALMERA
Soil Sampling Intercomparison Exercise (IAEA/SIE/01)

Paolo de Zorzi

APAT - Italian Environmental Protection Agency, Environmental Metrology Unit

Fourth IAEA ALMERA Network Meeting
ICTP, Trieste (Italy) 5-7 November 2007

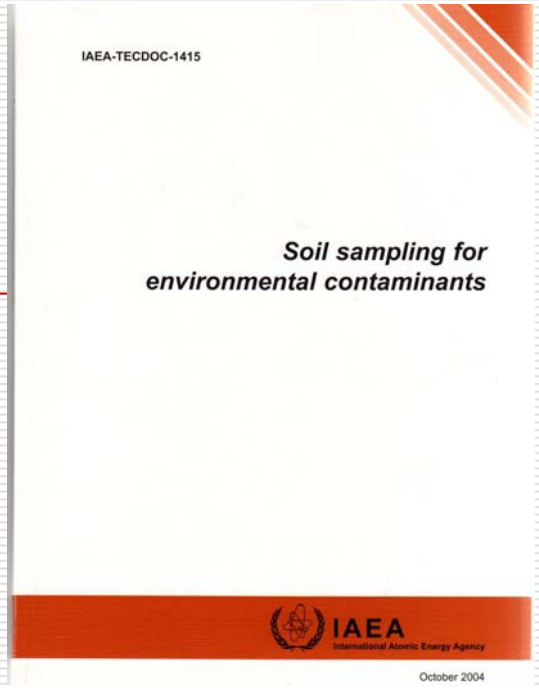
Background (1)

- Sampling is the basis for a correct measurement process
- Sampling is not a stand-alone operation; it is part of a chain of measurement.
- In soil analysis sampling can influences the final analytical data and it contributes to measurement uncertainty.
- Soil sampling for environmental monitoring is still a matter of debate. An increasing effort on metrological issues related to sampling is going on.

Background (2)

With reference to radionuclide monitoring activity "sampling" is considered a crucial issue

- IAEA-TECDOC-1415 (2004) "Soil Sampling for environmental contaminants"
- ICRU REPORT 75 (2006), "Sampling for Radionuclides in the Environment"



What is needed ?

- We need to improve the analytical data comparability at all level (environmental control and monitoring, research, etc.)
- Wide variety of sampling strategies & techniques adopted (also for the same objective);
- Inter-laboratory exercises are suitable tools to compare different measurement processes and to asses laboratories' performances

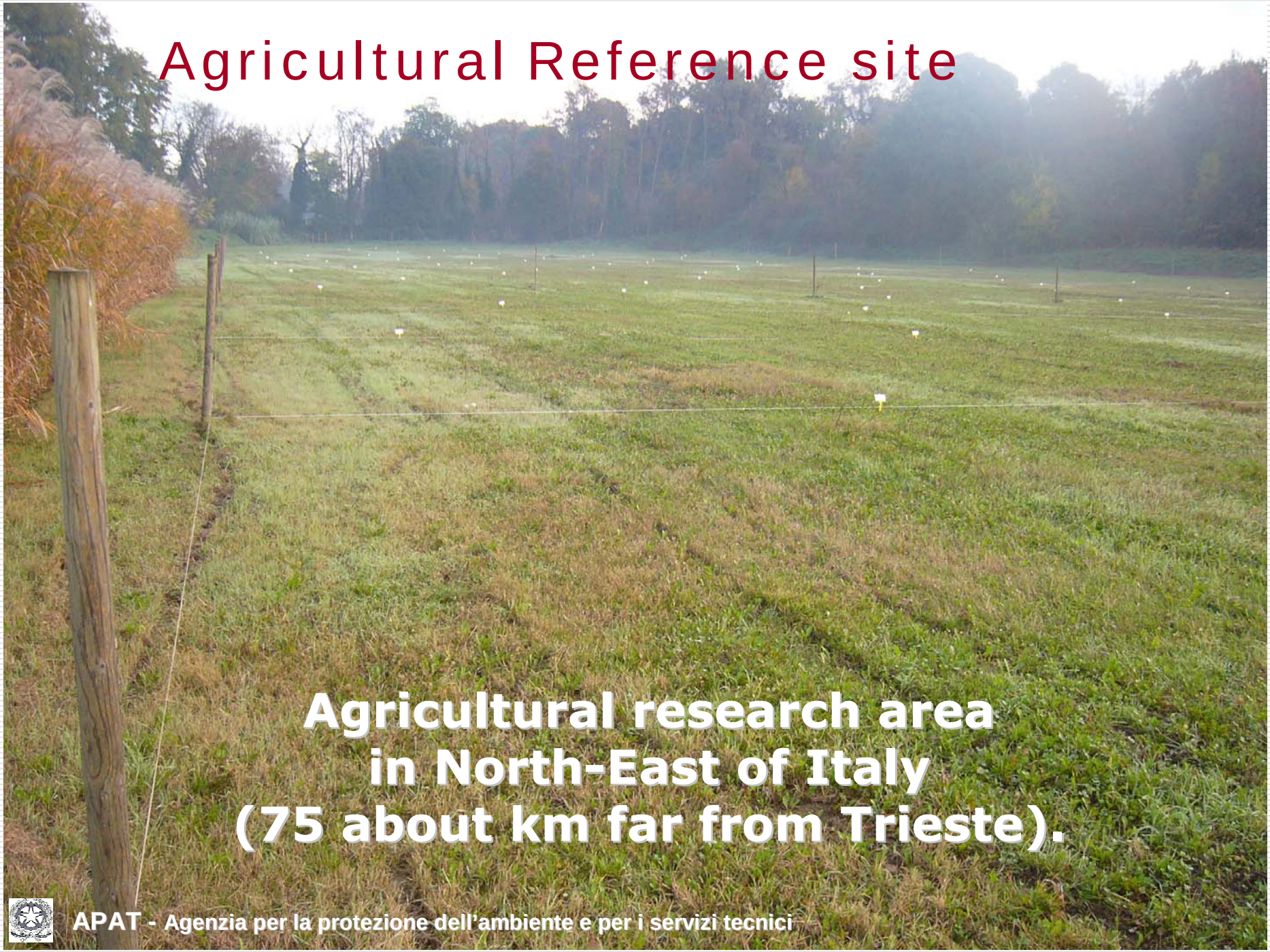
Are inter-comparison exercises applicable for sampling ?

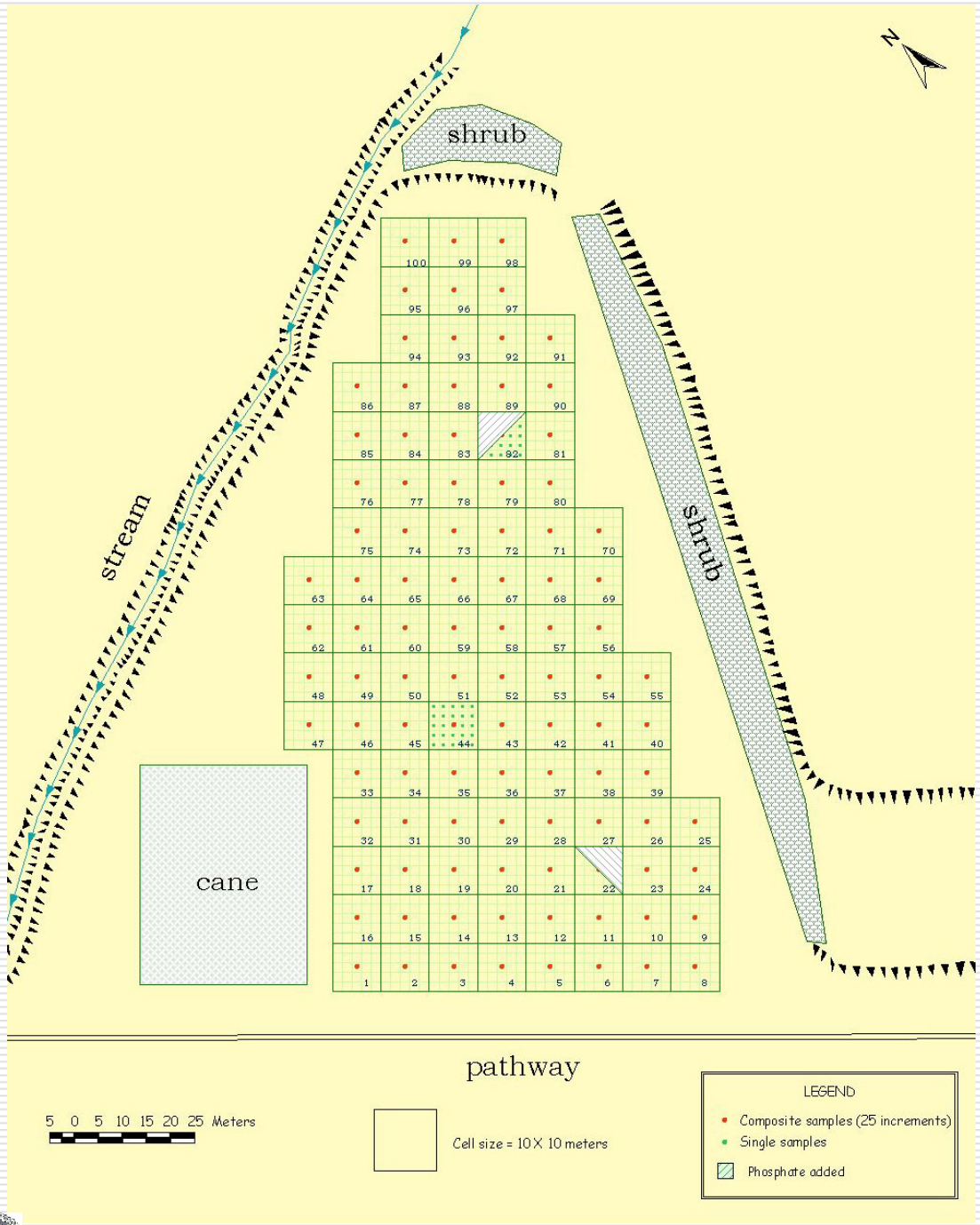
Some requirements for the analytical field

- Certified (or not certified) Reference Material (CRM-RM).
- Matrix similar to the target to be analysed.
- Assigned values and associated uncertainties.
- Homogeneity and stability.

Does it exist for sampling ?

Agricultural Reference site





Reference sampling

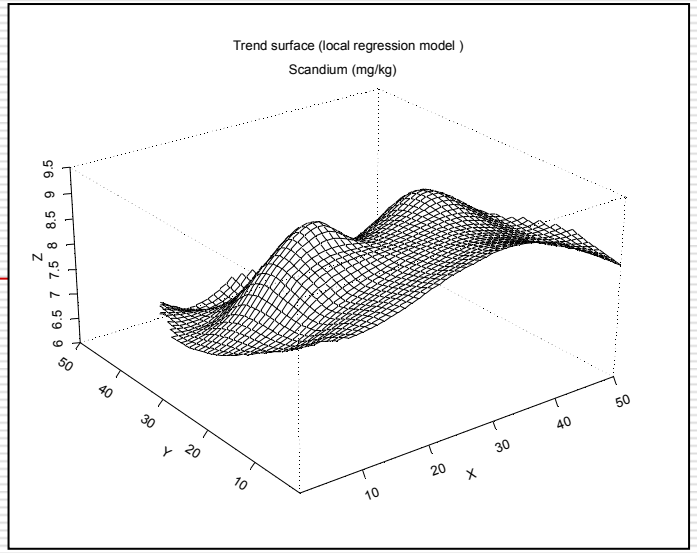
100 composite samples (pooling 25 increments per cell)

+

2 cells sampled again (collecting 25 single sample each)

Adapted from CEEM-soil project scheme:
- Desaules et al., 2001;
- Muntau et al., 2001;
- Wagner et al., 2001.

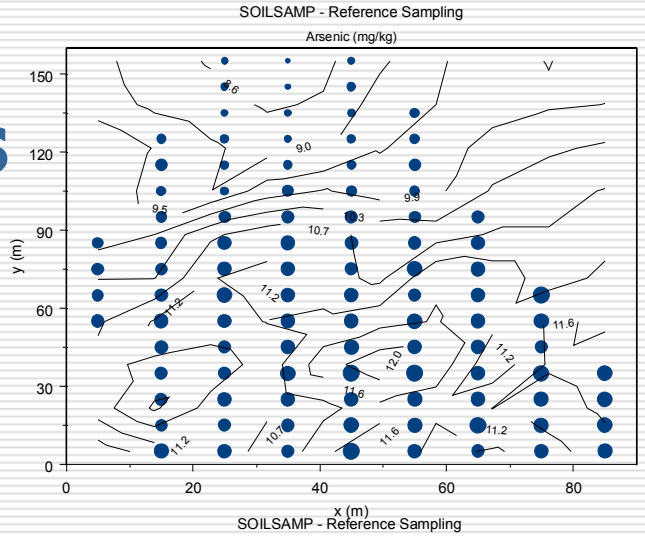
Reference site
Characterization



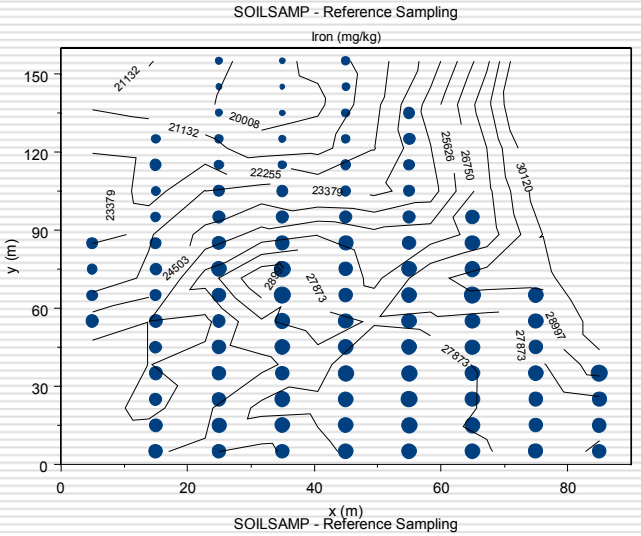
- Samples preparation;
- Analytical activity
  - Pedochemical properties (texture, C_{org}, N_{tot}, carbonate, P (tot and available), CEC, pH, exchangeable cations (Mg, Ca, K);
  - Particle size measurements;
  - Metals content by INAA measurements
- Geostatistical analysis

Spatial variation

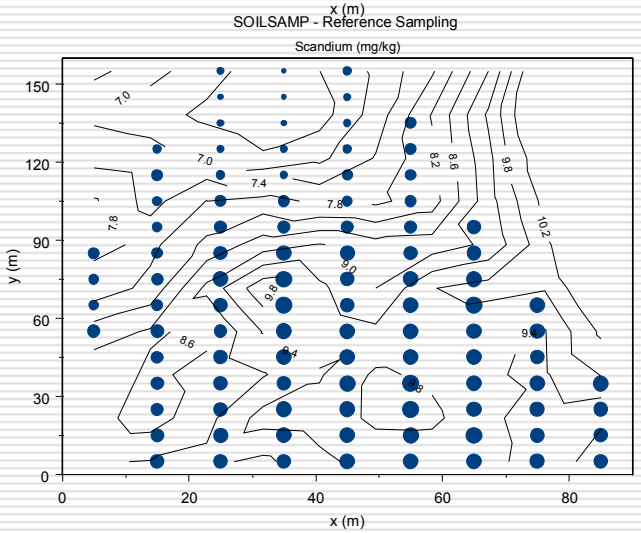
As



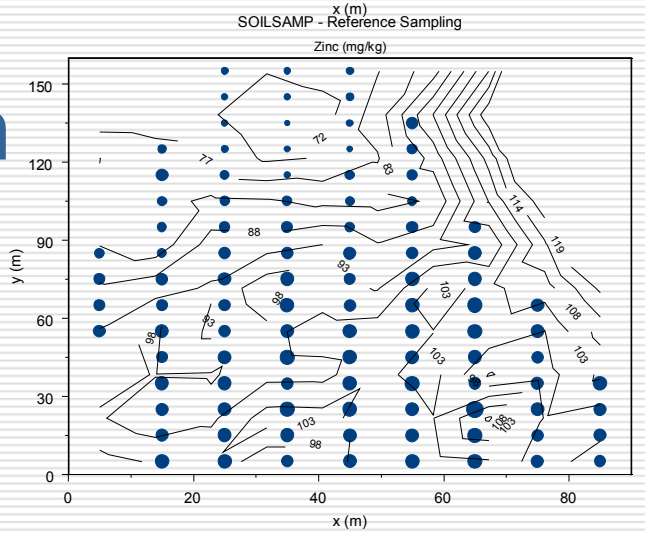
Fe



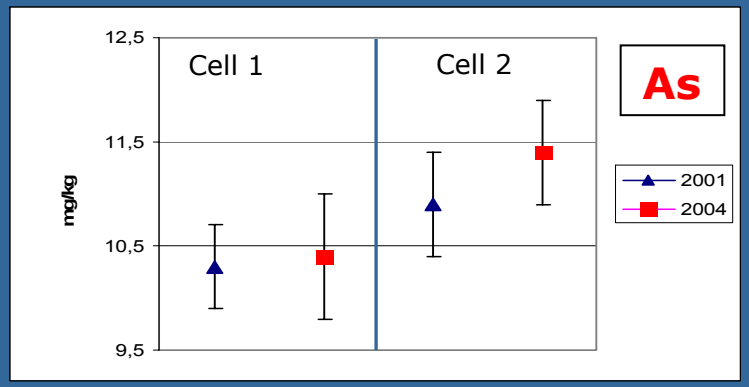
Sc

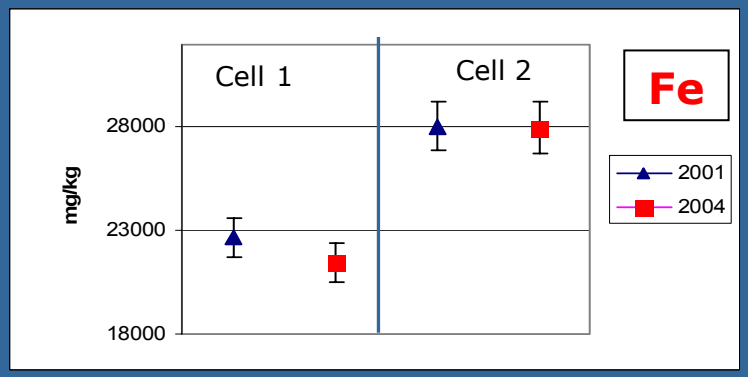


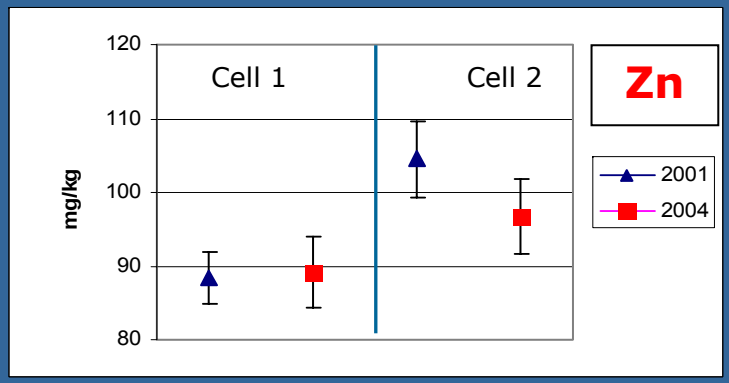
Zn

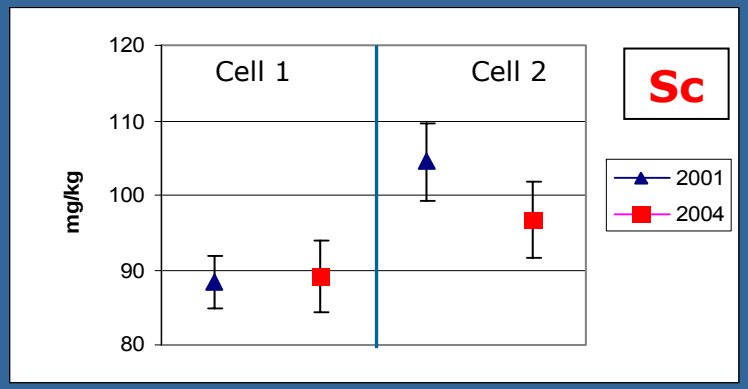


Temporal variability









No significant variability according to ISO Guide 33 criterion

$$X_{2001} - X_{2004} = \Delta_m < U_{\Delta_m}$$

Reference values – metal content

As	Fe	Sc	Zn
mg kg^{-1}			
10.6 ± 0.2	25570 ± 565	**8.6 ± 0.2**	**91.8 ± 2.1**

Uncertainty components

- Spatial variation of the metal content within the reference site;
- sampling, including the sampling operation (strategy, devices, sampler, etc.) and the sample preparation (from primary to test portion);
- analysis.

Applicability to radionuclides

Main assumptions:

- **Sampling for radionuclides in the environment is not unlike sampling for other attributes of environmental media**
- **Natural radioactivity of soil is largely controlled by the mineral composition of the parent material**
- **Most of the trace elements (metals and radionuclides) are fixed to the finer soil fractions as Sc**
- **Positive correlation of most radionuclides with metals:**
  - **Fe, Zn and Mn with ^{226}Ra and ^{232}Th**
  - **Sc are positively correlated with Fe (similar soil distribution pattern)**
- **Similar assumptions are reported in the IAEA TECDOC 2004**

IAEA/SIE/01

Participants

10 laboratories

Brazil

Mexico

Iran Syria Slovenia Hungary Slovakia

Korea

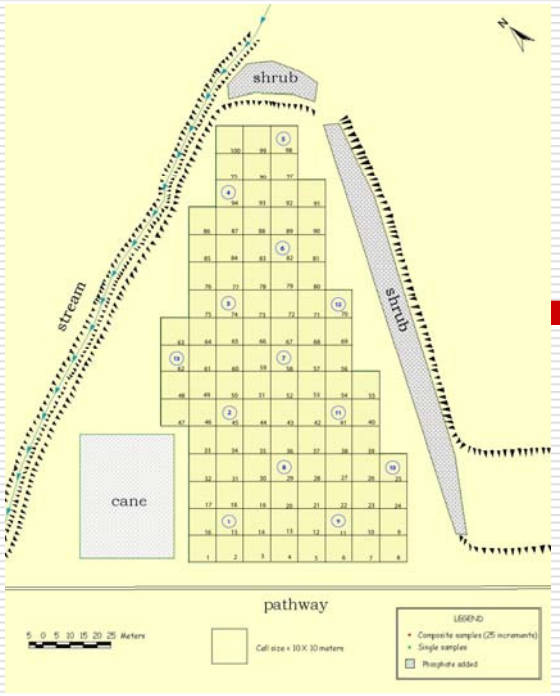
Lithuania

Ukraine

Object the interlaboratory exercise
IAEA/SIE/01

- Soil sampling aimed at determining the concentration mean value of several radionuclides within an area of 10000 square meters.

- Radionuclides: ^{90}Sr, Pu, ^{241}Am, ^{238}U



General rules and instructions (1)

Two days on the field (November, 16-17, 2005)

- Each sampling team was asked to apply its own sampling techniques and strategies with the same care usually taken.

General rules and instructions (2)

- Each sampling team could deliver not more than 15 samples (laboratory samples) of at most 1 liter.

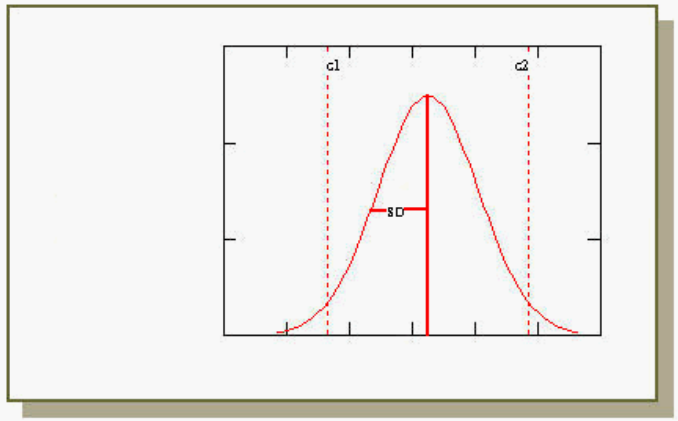
- The laboratory sample can be obtained by:
  - ✓ "composite sample" or "single sample"

- Soil samples should be collected at most within 40 cm on depth (ploughed layer);

- Maximum time allowed (3 hours)

General rules and instructions (3)

- The laboratory samples were delivered to IAEA at the end of the activity on the field.
- Sample preparation and analyses were carried out by a single laboratory following a stated protocol.
- Analytical technique for trace element (INAA) requires little or no sample processing.



Data assessment (1)

The participant's data were assessed:

- according to ISO13258:2005 (E) *"Statistical methods for use in proficiency testing by inter-laboratory comparison";*
- On the basis of operational aspects (expert judgment)

Data assessment (2)

Bias $$D = X_{PAR} - X_{REF}$$

Score $$\zeta = \frac{X_{PAR} - X_{REF}}{\sqrt{u_{PAR}^2 + u_{REF}^2}}$$

X_{PAR} = Participant's mean value for each measurand;

X_{REF} = Reference value assigend to each measurand of the reference site;

u_{REF} = Experimental standard uncertainty assigned to the reference value expressed as experimental standard deviation of the mean;

u_{PAR} = Participant experimental standard uncertainty.

Data assessment (3) *Bias*

$\|D\| \leq 2$	**Suitable strategy**
$2 < \|D\| \leq 3$	**Warning/Questionable**
$\|D\| > 3$	**Action**

$\hat{\sigma}$ = robust standard deviation (n=10 meas)
of the interlaboratory exercise IAEA/SEI/01

Data assessment (4)

ζ score

$\hat{\sigma}$

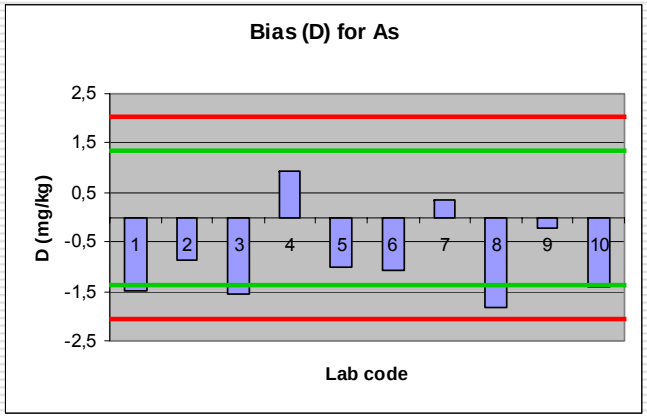
$\lvert\zeta\rvert \leq 2$	**Suitable strategy**
$2 < \lvert\zeta\rvert \leq 3$	**Warning/Questionable**
$\lvert\zeta\rvert > 3$	**Action**

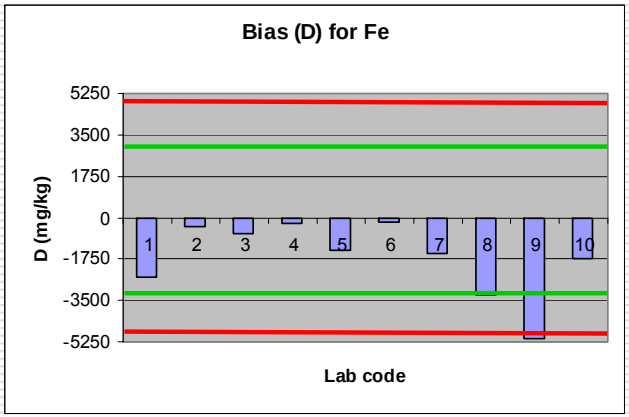
Results (1)

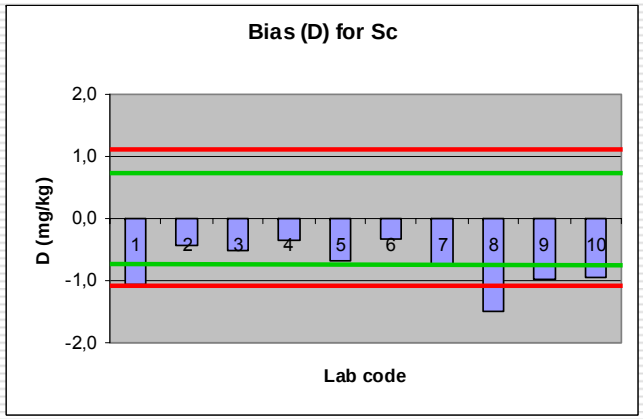
In a homogeneous agricultural area the **sampling strategies** chosen by the laboratories **are comparable**

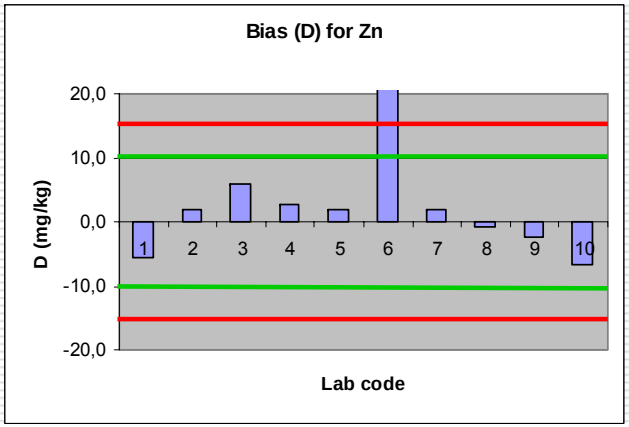
- In terms of Bias:
  - ✓ at most **10 %** of the labs show absolute values **>3**σ;
  - ✓ **60-90 %** of the values are **≤2**σ (suitable strategy)
- In terms of ζ-score:
  - ✓ **at most 40 %** (only for As) the score values **>3**;
  - ✓ **40-80 % ≤2**

Bias

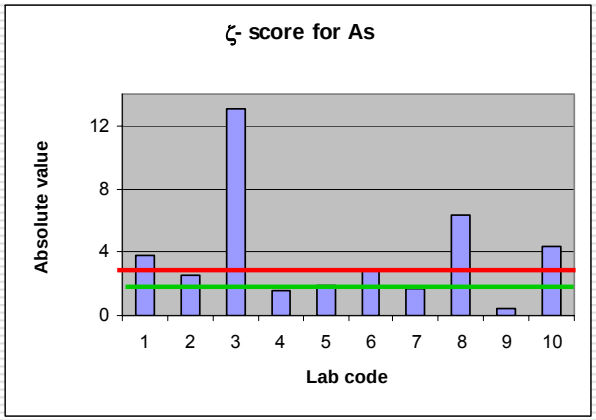

Bias (D) for As
D (mg/kg)
2,5
1,5
0,5
-0,5
-1,5
-2,5
1
2
3
4
5
6
7
8
9
10
Lab code

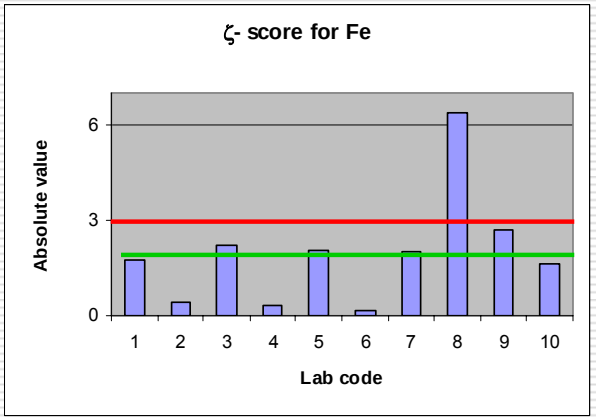

Bias (D) for Fe
D (mg/kg)
5250
3500
1750
0
-1750
-3500
-5250
1
2
3
4
5
6
7
8
9
10
Lab code

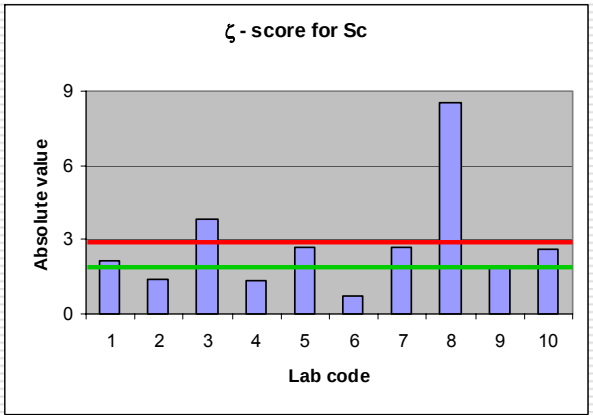

Bias (D) for Sc
D (mg/kg)
2,0
1,0
0,0
-1,0
-2,0
1
2
3
4
5
6
7
8
9
10
Lab code

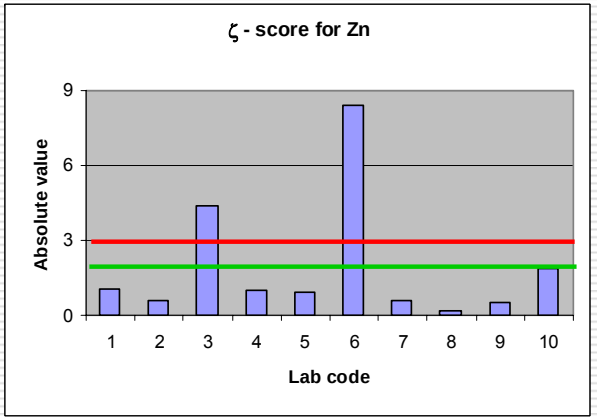

Bias (D) for Zn
D (mg/kg)
20,0
10,0
0,0
-10,0
-20,0
1
2
3
4
5
6
7
8
9
10
Lab code

ζ-score


ζ- score for As
Absolute value
0
4
8
12
1 2 3 4 5 6 7 8 9 10
Lab code


ζ- score for Fe
Absolute value
0
3
6
1 2 3 4 5 6 7 8 9 10
Lab code


ζ - score for Sc
Absolute value
0
3
6
9
1 2 3 4 5 6 7 8 9 10
Lab code


ζ - score for Zn
Absolute value
0
3
6
9
1 2 3 4 5 6 7 8 9 10
Lab code

Results (2)

- Sampling of top soil in arable and ploughed land is relatively easy leading to comparable results between different sampling procedures

- In this case, operational aspects of the different sampling procedures are significative:
  - Type of samples;
  - Number of samples/increments;
  - Time dedicated;
  - Effort.

Lab code	Sampling pattern	Sampling devices	Type of sample	Sample Pretreatment in the field	Number of laboratory samples (1)	Number of increments (2)	Time (3)	Effort	Operational Remarks (4)
Korea *(1 ampler)*	Non systematic *Zig-zag*	Sampling rings	**Composite**	**No**	**	**	*	**	**
Brasil *(1 ampler)*	Systematic	Shovel / Spatula	**Single**	**Yes**	*	-	**	*	*
Slovenia *(2 amplers)*	Systematic *Random (vertical)*	Corer	**Single**	**No**	*	-	**	*	*
Lithuania *(1 sampler)*	Non Systematic	Spatola / Spade	**Single**	**No**	*	-	***	**	**
Slovakia *(2 samplers)*	Systematic	Shovel	**Single**	**Yes**	*	-	**	**	**
Ukraine *(2 samplers)*	Stratified random	Corer	**Composite**	**No**	**	***	**	*	**
Mexico *(1 sampler)*	Systematic	Corer	**Composite**	**Yes**	*	**	**	***	**
Iran *(1 sampler)*	Systematic	Shovel	**Composite**	**Yes**	*	***	**	**	**
Hungary *(2 samplers)*	Stratified random	Corer	**Single**	**No**	*	-	***	**	**
Syria *(1 sampler)*	Non Systematic	Spatula/Scoop	**Composite**	**No**	**	***	**	***	***

1) N° of Laboratory samples = *** (1-5), ** (6-10), * (11-15)

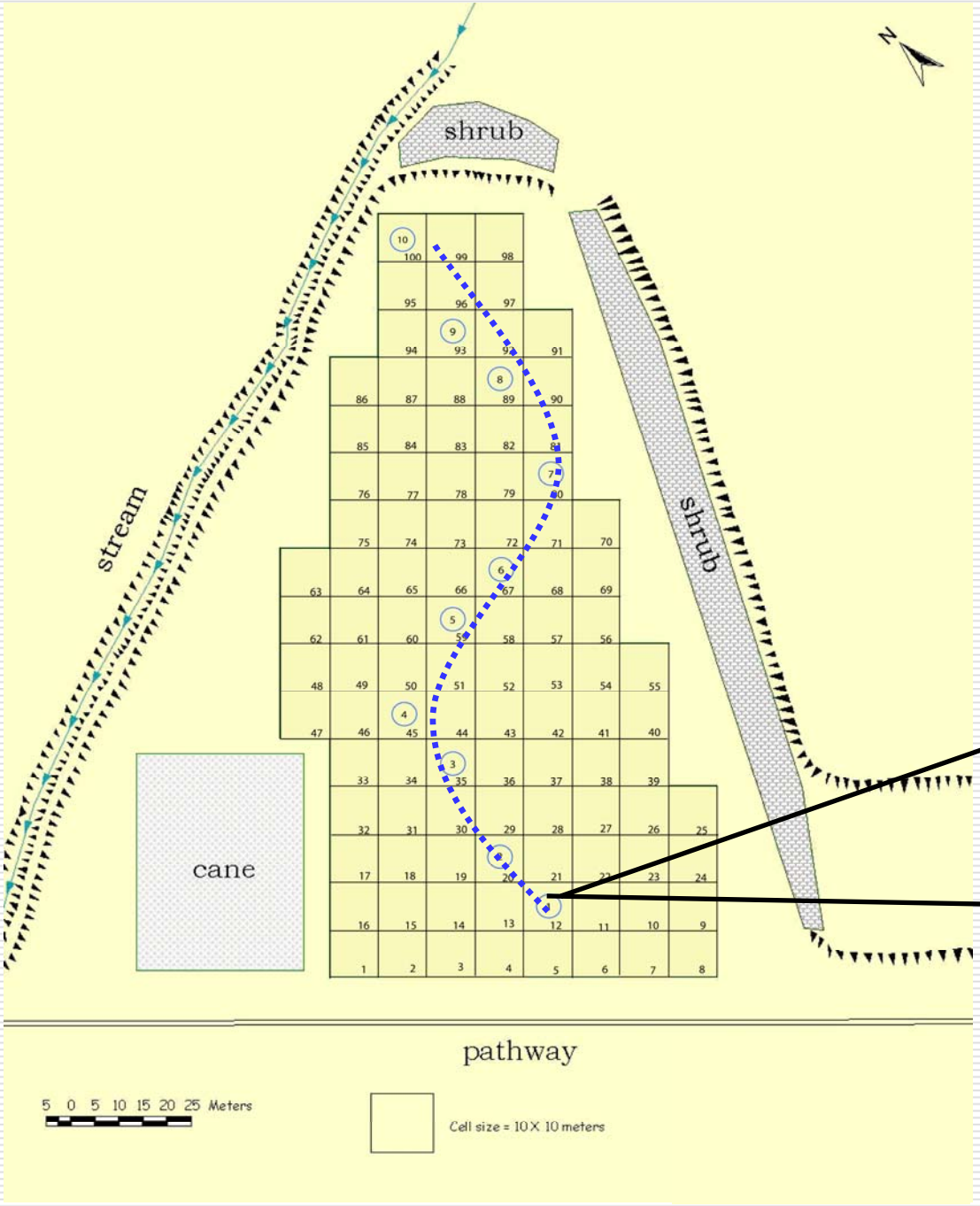
2) N° of increments = *** (1-5), ** (6-10), * (> 11)

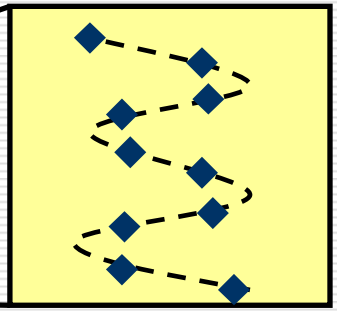
3) Time (minutes) = *** (≤ 90); ** (91-180); * (> 180)

4) The higher number of asterisks (*) the better judgment and operational performance

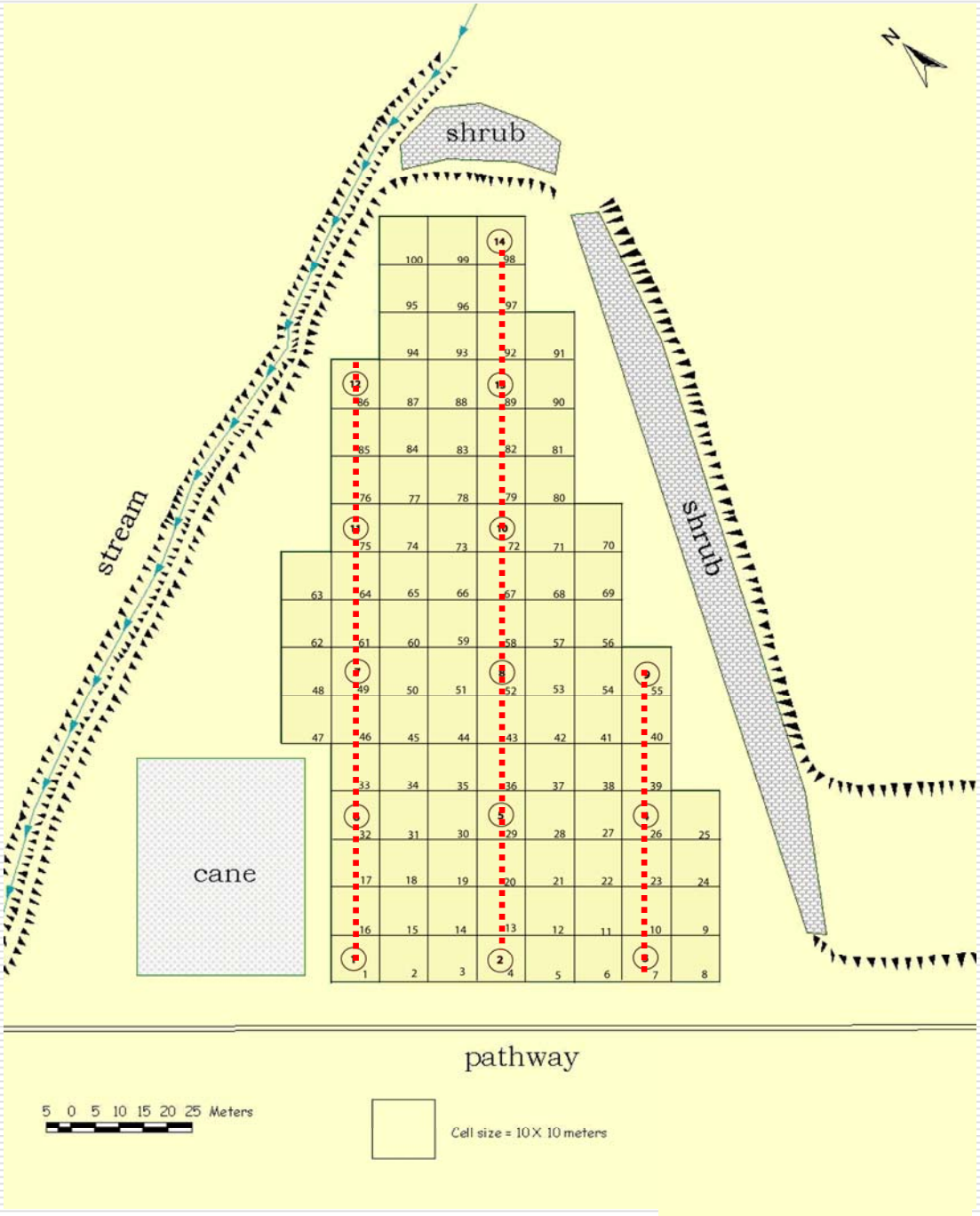
How did the laboratories sample ?

- Three main **sampling strategies/patterns**:
  - Systematic (transect, triangular grid, diagonal): **5 labs**;
  - Stratified random: **2 labs**;
  - Non-systematic/irregular: **3 labs**.

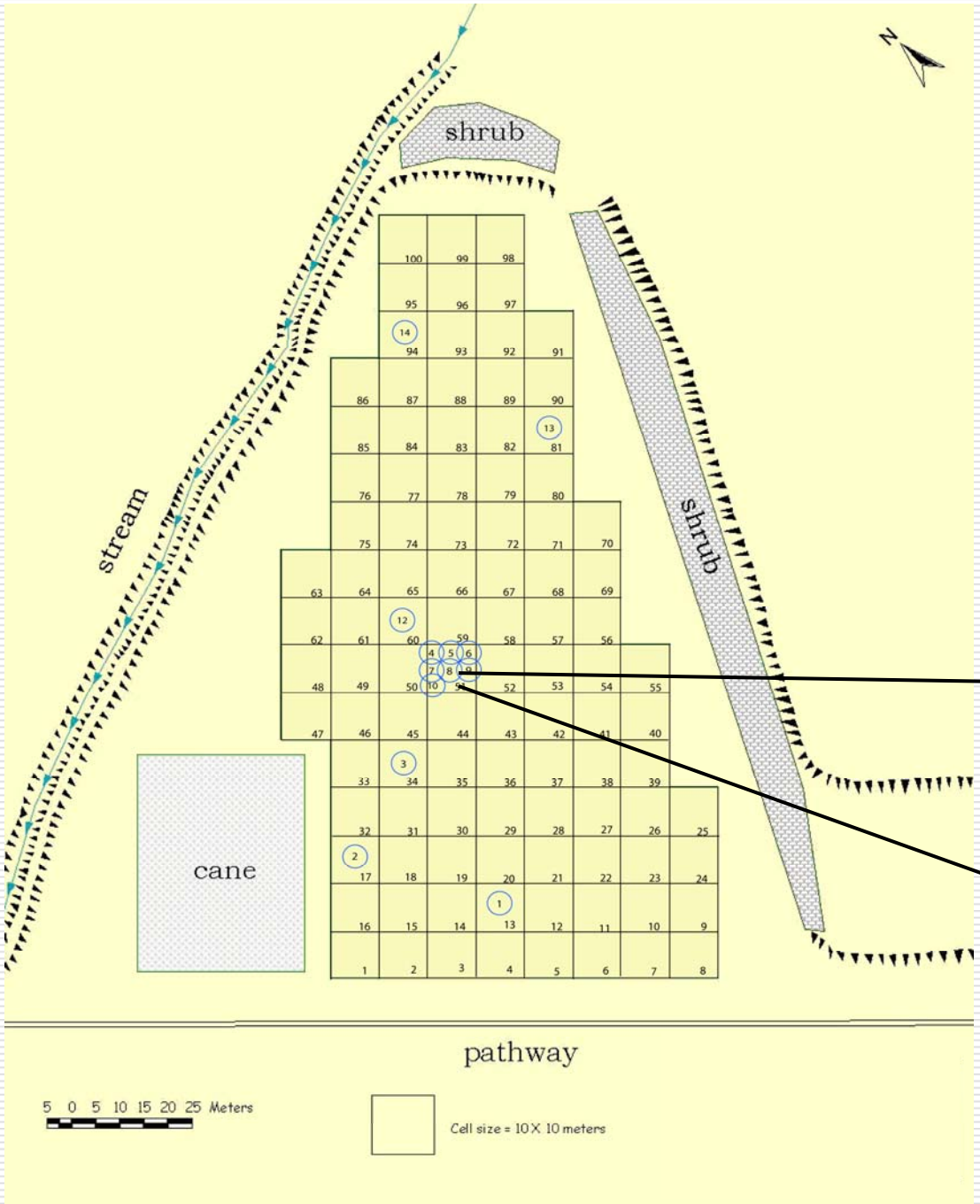




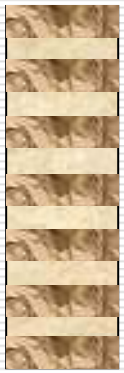
Irregular:
(zig-zag)

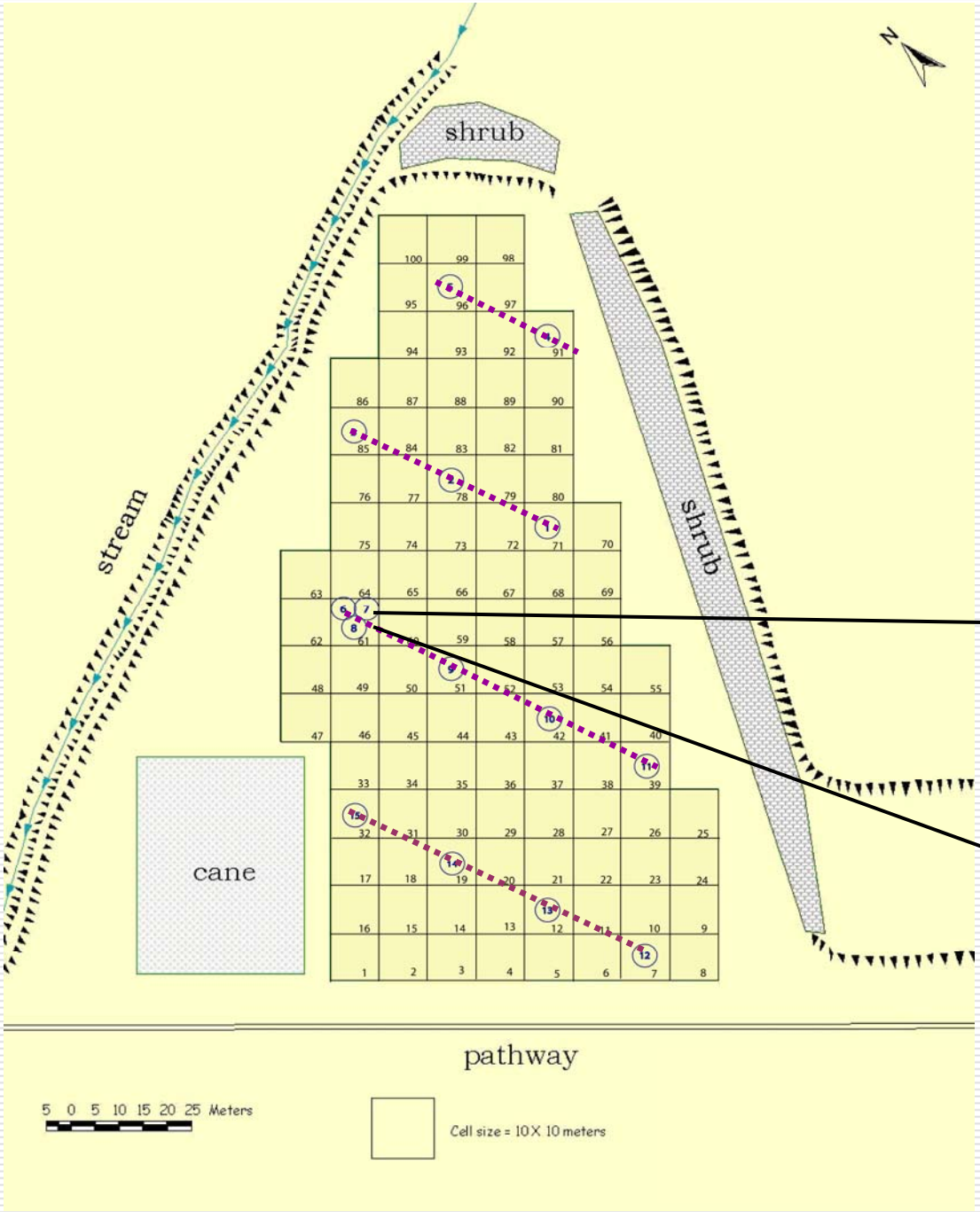


Systematic: (transect)

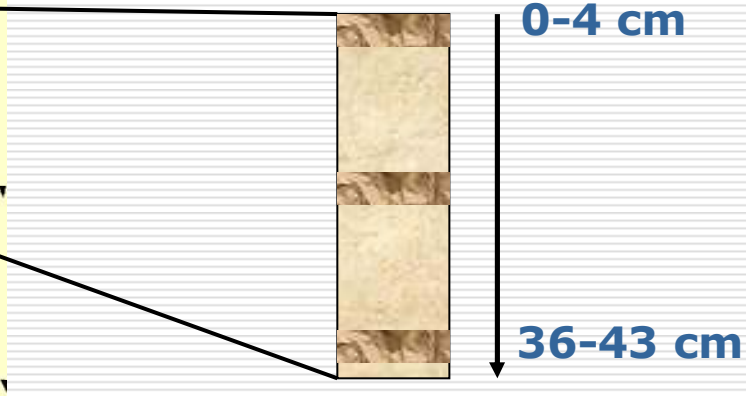


Stratified random





Systematic: (diagonal)



shovel

corer

scoop

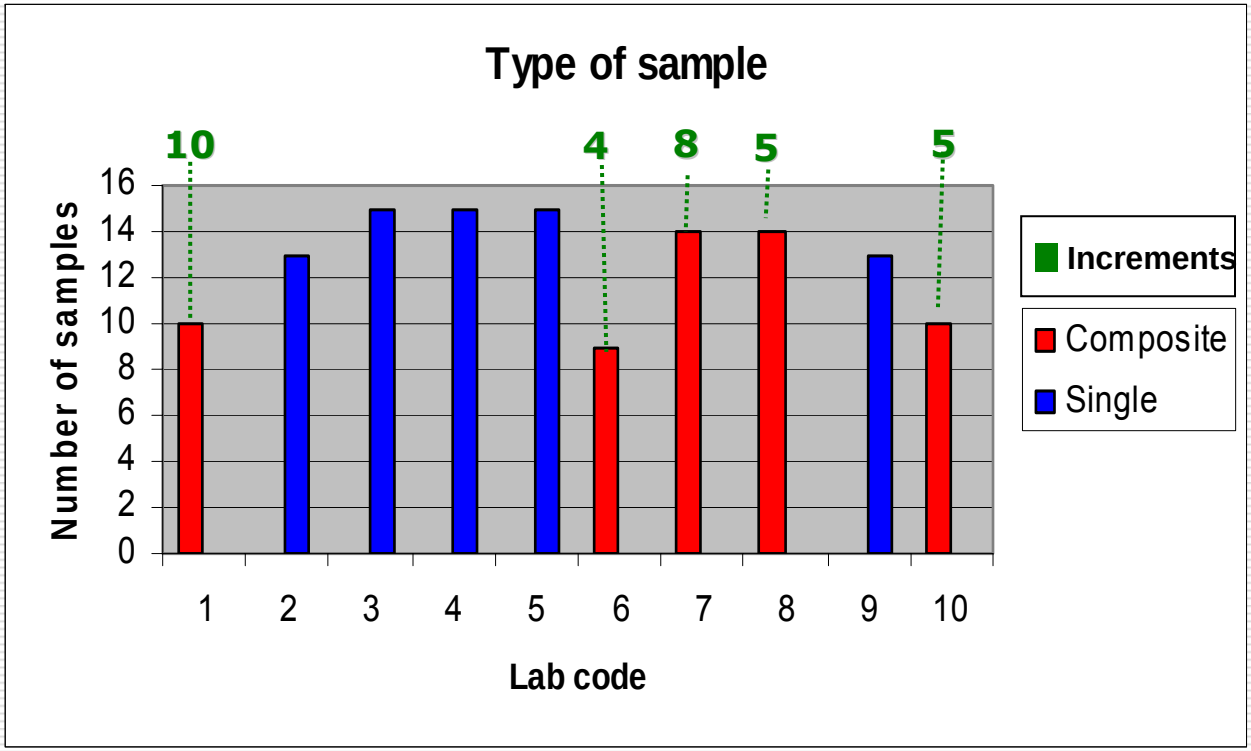
corers


rings


shovel


spatula

Type of samples



5 composite (increments 4-10)

5 singles (13-15)

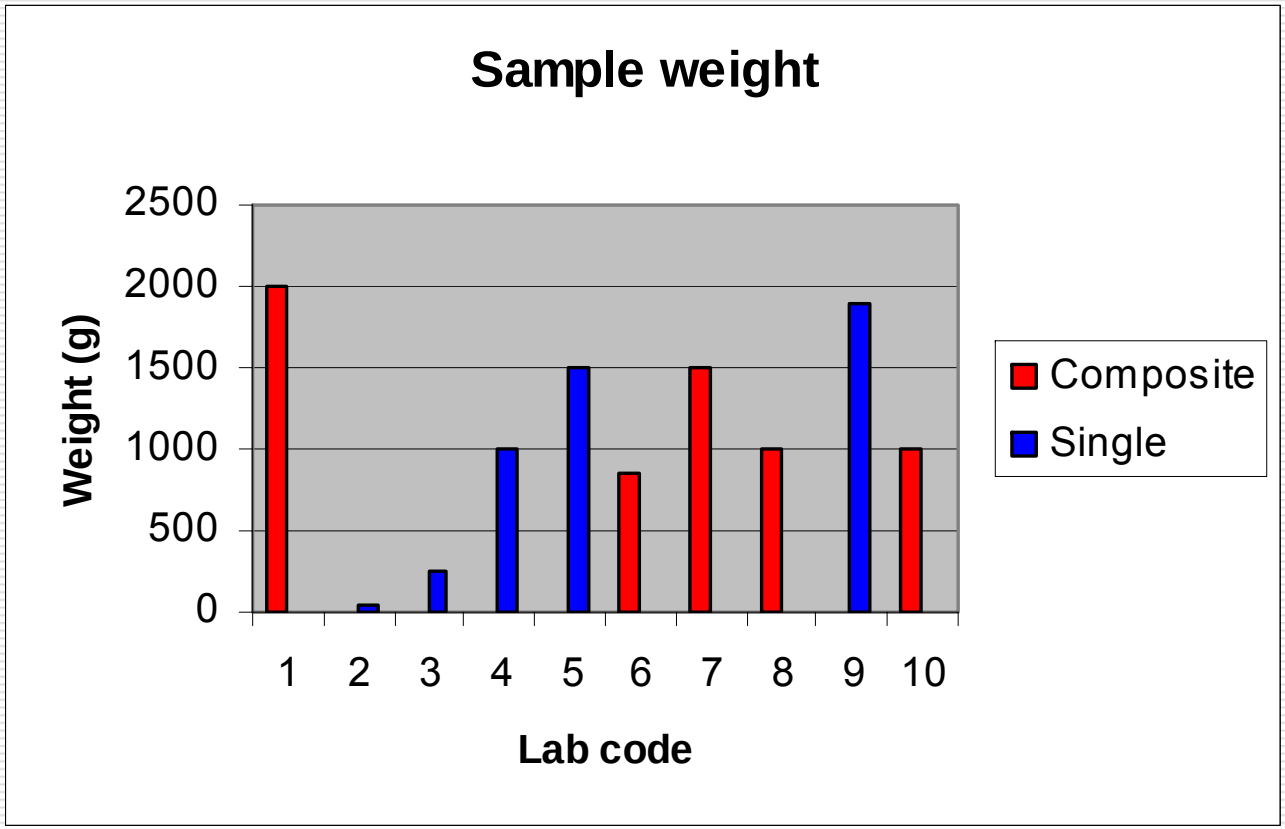
Sample preparation in the field

- Cutting vegetation;
- Removing stones and roots;
- Sieving (2 mm)
- Quartering and mass reduction.

Effect on the measurement results

- Measurement results and associated uncertainties can be influenced even by:
  - Samples size (volume, mass);
  - Sampling depth (top soil or deeper).

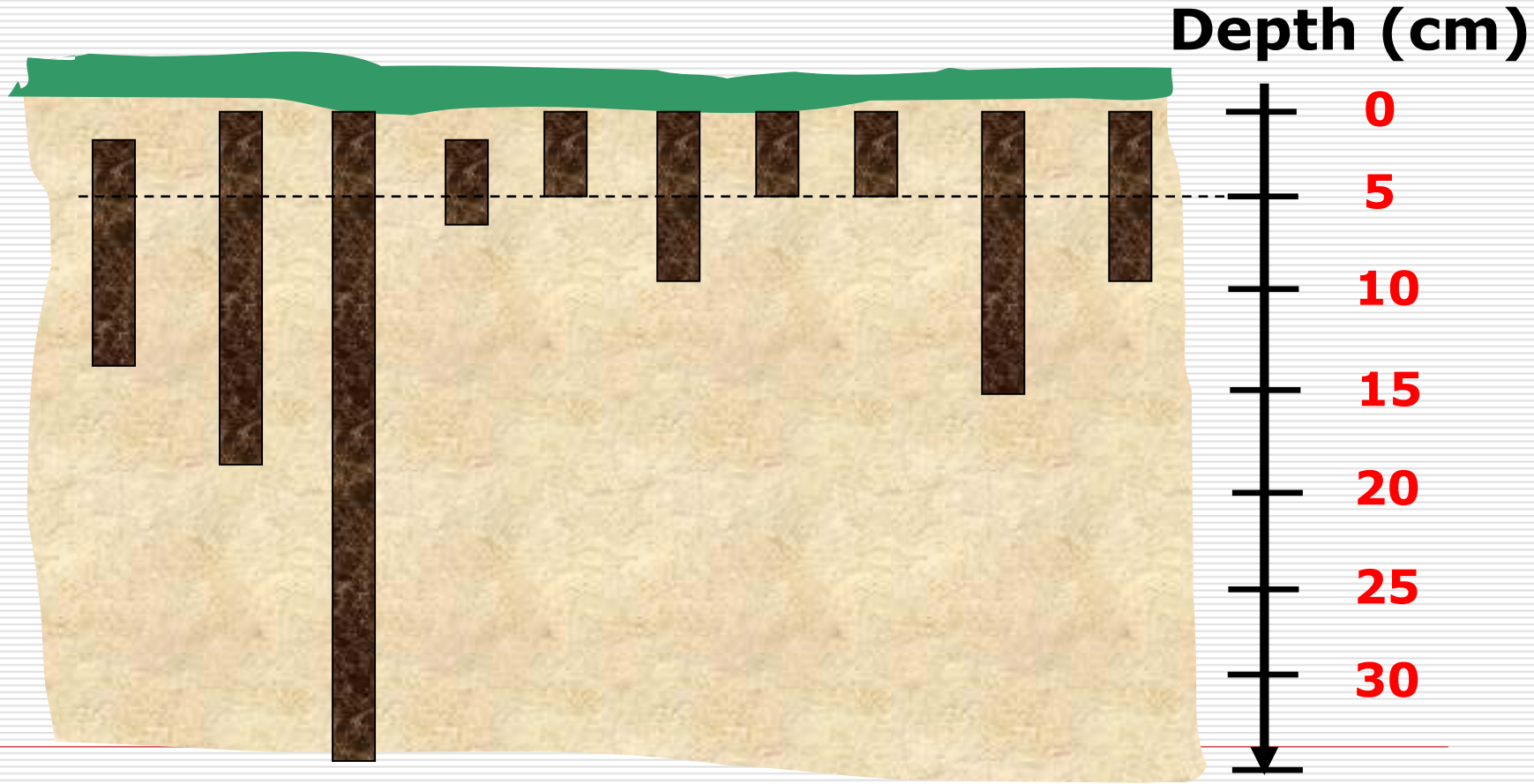
Sampling weight



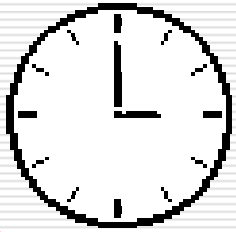
Composite
(850-2000 g)

Single
(50-1900 g)

Sampling depth

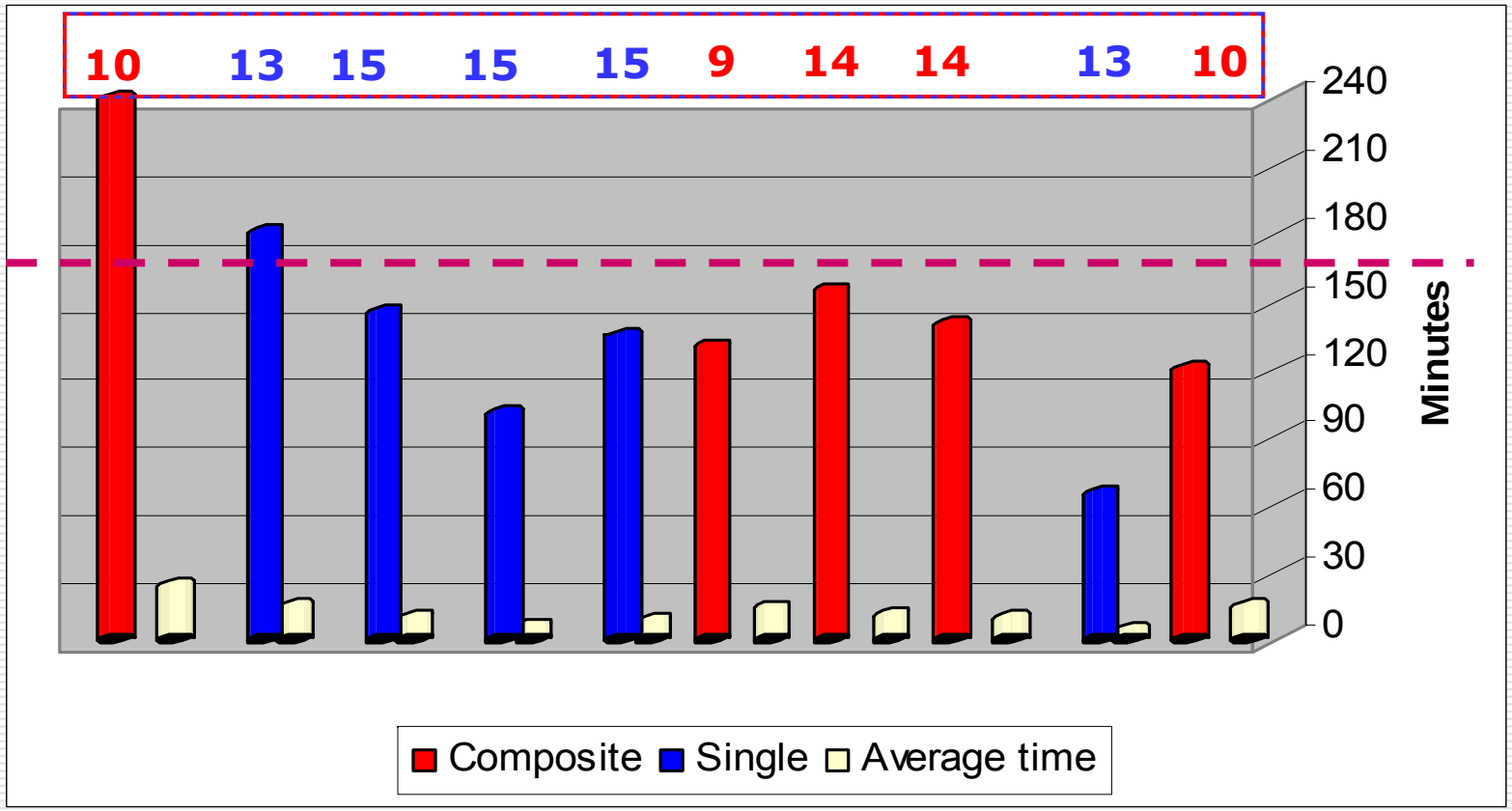


Sampling time



Maximum time: 3 hours

Number of samples



General remarks (1)

- For easy environments, such as an agricultural field, sampling procedure and strategy should be simple;
- The observed homogeneous distribution of the trace element (horizontal and vertical) do not justify intensive sampling (high number of samples/increments)
- Intercomparison results confirm, on the basis of experimental data, what was probably intuitive.

Future
of the Reference Site concept

- Tests on more heterogeneous area (semi-natural or contaminated);
- Identification of hot-spots

- **Heterogeneity** = necessary for testing on soil sampling strategies;
- **Spatial variation** = replace the term "*homogeneity*" in the definition of "Reference Site";
- **Temporal variability** = replace the term"*stability*" in the definition of "Reference Site"
- **Homogeneity** = fundamental requirements for RM in chemical analysis

Literature references

- de Zorzi et al. (2002), *"A practical approach for assessment of sampling uncertainty".* Accred. Qual. Assur. ,7- pp 182-188
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- de Zorzi et al. (2007) *"Estimation of uncertainty arising from different soil sampling devices: the use of variogram parameters",* Chemosphere (in press);
- de Zorzi et al. (a) (2007), "*A soil sampling reference site: the challenge in defining reference material for sampling"* J. Rad. Isotope (in press);

For further information

Paolo de Zorzi

APAT

Via Castel Romano, 100 – 00128 Rome (Italy)

Phone: +39-06-50073211-50073206

E-mail: paolo.dezorzi@apat.it

Thank you for your attention !