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Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

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Estimation of Uncertainty arising from Sampling - Exercise

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Estimation of Uncertainty arising from Sampling
using variogram parameters

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Workshop on
"Understanding and Evaluating Radioanalytical Measurement Uncertainty“

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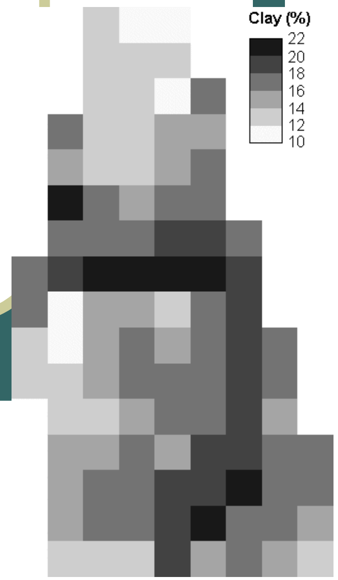

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Environmental Data

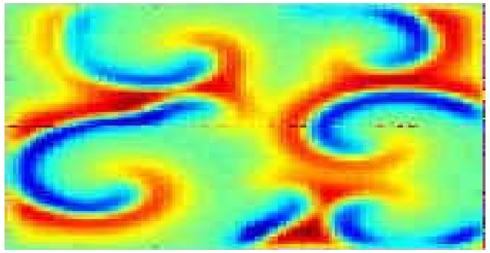
- Besides the effects of sampling techniques, sample preparation/reduction, and laboratory analyses, the data also differ because of spatial variation
- Geostatistics enables us to quantify the spatial structure of a measured element separate from the total variance of the data

Geostatistics (1)

According to geostatistics and the regionalized variable theory, we assume that a variable (Z) is the sum of three components

$$Z(x) = m(x) + r(x) + \varepsilon$$

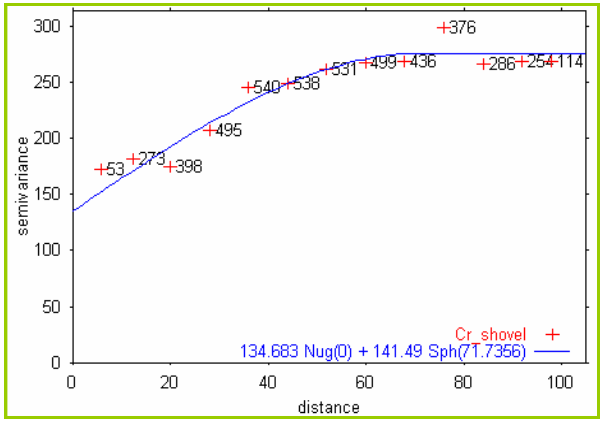
m = structural component
r = spatial correlated component (residual from m(x))
ε = uncorrelated random noise
x = location

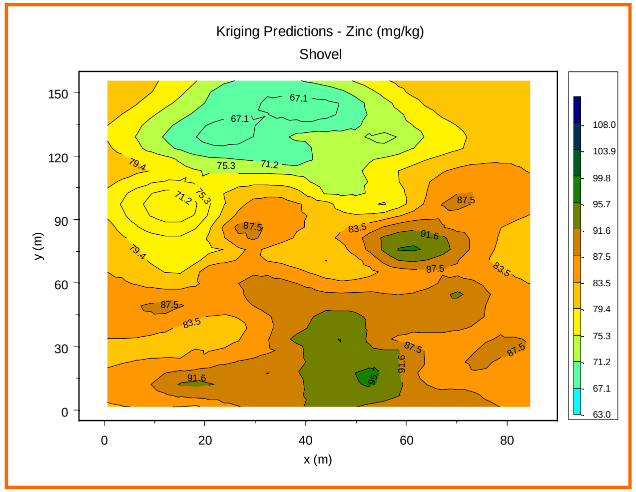


Geostatistics (2)

Geostatistical analysis include two phases:

- spatial modelling (variography);
- spatial interpolation (kriging)





The Experimental Variogram

$$\hat{\gamma}(h) = \frac{1}{2n} \sum_{i=1}^{n} \{z(x_i) - z(x_i + h)\}^2$$

The spatial correlated component and the noise term are encapsulated in an experimental variogram

- *RANGE*

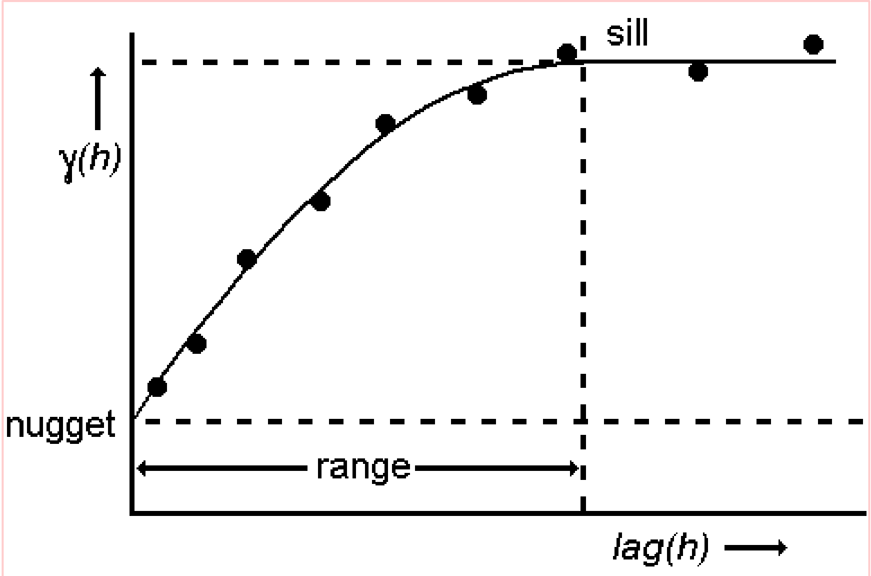
distance beyond which there is no correlation among variables

- *SILL*

value that variogram tends to when distances get very large

- *NUGGET*

measurement uncertainties and/or microscale variations that occur over distances less than the shortest sampling interval



Uncertainty from Sampling (1)

Total variance

$$s^2_{tot} = s^2_S + s^2_T + s^2_A + s^2_{SP}$$

- ✓ s^2_{tot} comprises:
  - ✓ the variances of sampling $\mathbf{s^2_S}$,
  - ✓ sample treatment/reduction $\mathbf{s^2_T}$,
  - ✓ analysis $\mathbf{s^2_A}$
  - ✓ and the spatial variability $\mathbf{s^2_{SP}}$

According to Geostatistics:

↓

The **nugget** variance includes variances due to:

- Sampling
- Analysis
- Spatial correlation that occur over distances less then the shortest sampling interval

→ **Measurement uncertainty**

Uncertainty from Sampling (2)

$$s^2_{\text{nugget}} = s^2_{\text{analysis}} + s^2_{\text{sampling}} + s^2_{\text{sample reduction}}$$

Transponing:

$$s^2_{\text{sampling}} = s^2_{\text{nugget}} - (s^2_{\text{analysis}} + s^2_{\text{sample reduction}})$$

$$s^2_{\text{analysis}} + s^2_{\text{sample reduction}}$$

May be calculated together experimentally analysing replicates (test portions) taken from independent test samples

$$s^2_{\text{nugget}}$$

is determined by geostatistics

Uncertainty from Sampling (3)

The **sampling standard uncertainty** is:

$$u_{sampling} = \sqrt{s^2_{sampling}}$$

As **uncertainty relative** to the mean mass fraction of an element becomes:

$$u\%_{sampling} = (u_{sampling} / x_{mean})*100$$

The **sampling expanded uncertainty** is:

$$U_{sampling} = ku_{sampling} \quad (k = 2)$$

Applicability and assumptions

- Suitable data set: at least **30-100 samples** data value;
- The higher the number of samples the more accurate the fitted model;
- **No correlation** between analytical and sampling variance
- **Subjective assumptions** regarding the model for the experimental variogram
- **Repeatability** of sampling operation

Example:
Variogram parameters

Scope: Estimate the $u_{sampling}$, due to different soil sampling devices.

- 10000 square meters reference site;
- Hand auger, mechanical auger, shovel
- Comparative sampling (sistematic random sampling);
- 105 test samples from 105 primary samples (each sampling device);
- Sample preparation and analysis by k0-INAA (Zn mean concentration value) carried out by a single lab.

Comparative sampling

105 single samples collected by 3 sampling devices

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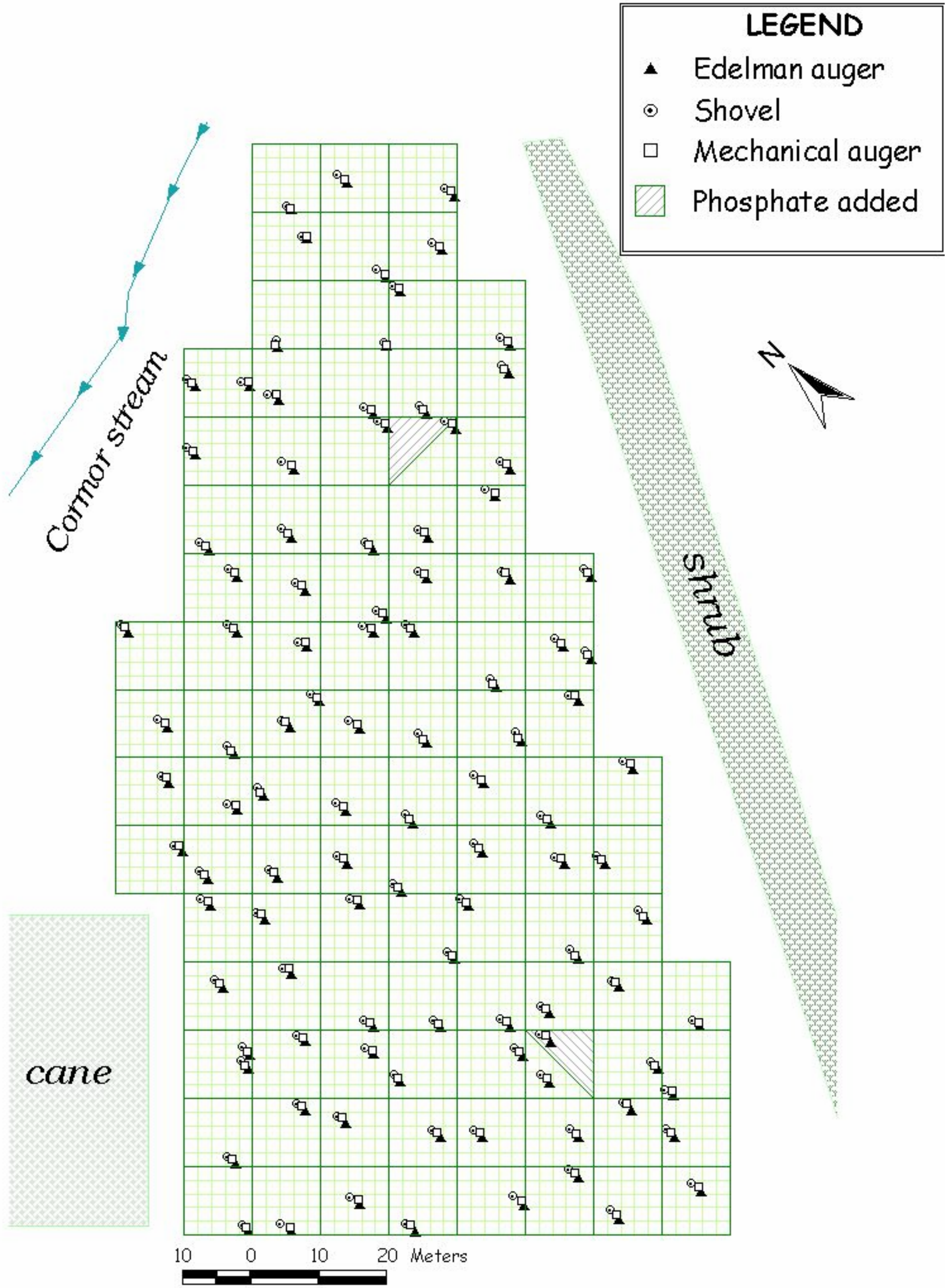
Data set of 105 values for each device

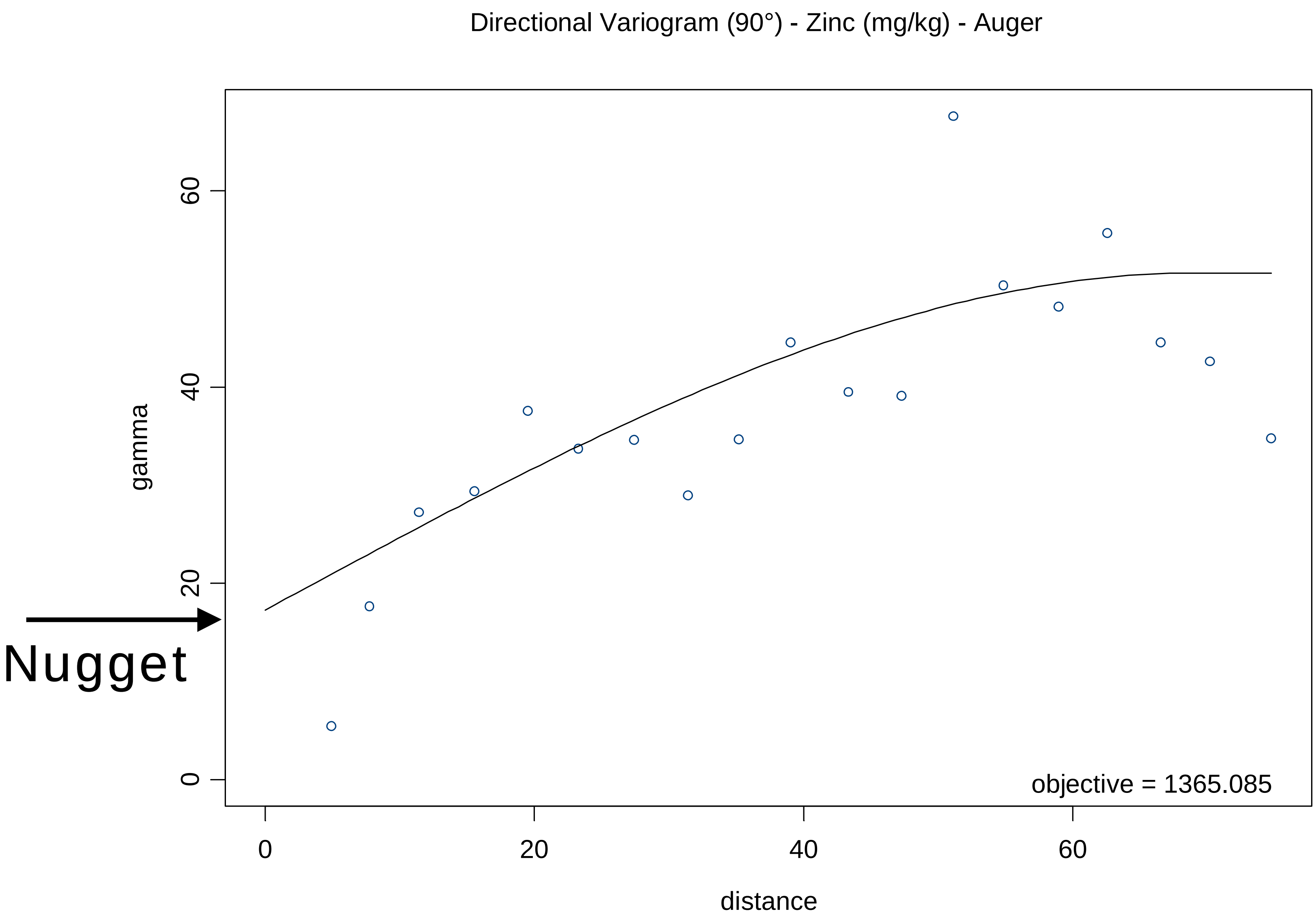


Hand auger

Mechanical auger

Shovel

Variogram parameters



Calculation (1)

$$s^2_{sampling} = s^2_{nugget} - (s^2_{analysis} + s^2_{sample\ reduction}) =$$

17,3 – 4,1 = 13,2

$s^2_{analysis} + s^2_{sample\ reduction}$

Were calculated together experimentally analysing 10 replicates (test portions) taken from 3 independent test samples

Calculation (2)

The **sampling standard uncertainty** is:

$$u_{sampling} = \sqrt{s^2_{sampling}} = \sqrt{13,2} = 3,6 \text{ mg/kg}$$

As **uncertainty relative** to the Zn mean concentration (90,2 mg/kg) becomes:

$$u\%_{sampling} = (3,6 / 90,2)*100 = 4\ \%$$

The **sampling expanded uncertainty** is:

$$U_{sampling} = k* 3,6 = 7,3 \text{ mg/kg} \quad (k = 2)$$

$u_{sampling}$ vs. u_{meas}

⬇

Measurement standard uncertainty (from nugget value**)**

u_{meas} = 4,2 mg/kg

Sampling uncertainty (subtracting analytical uncertainty from meaurement uncertainty**)**

$u_{sampling}$ = 3,6 mg/kg

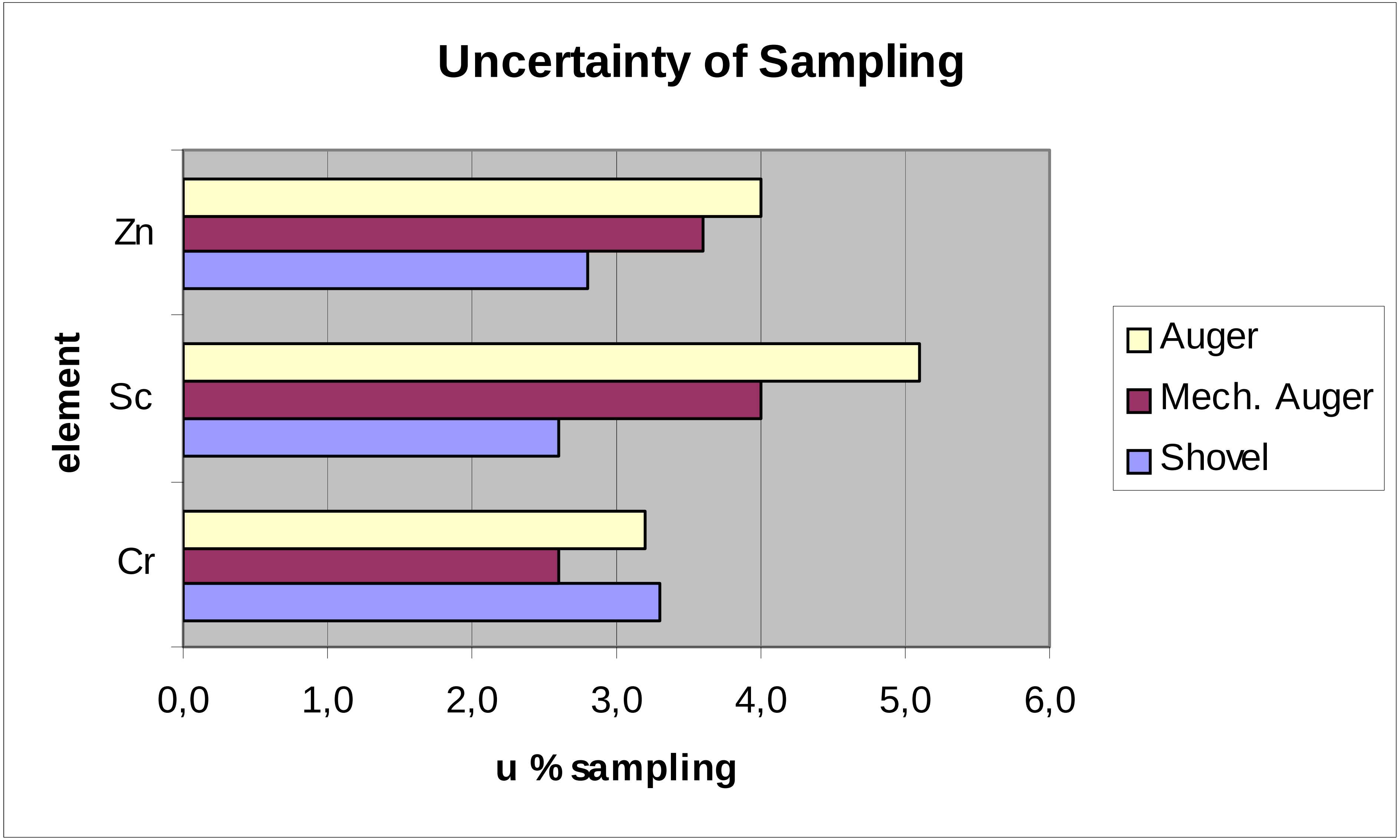
The contribution of the sampling to the measurement uncertainty is:

$$u\%_{s/meas} = (3,6/4,2)*100 = \mathbf{76\ \%}$$

Uncertainty budget

Zinc	Auger
Element mean value (n=105) x_{mean} (mg kg^{-1})	90,2
Nugget variance: s^2_{nugget}	17,3
Analytical variance: $s^2_{analytical}$	4,1
Sampling variance: $s^2_{sampling}$	13,2
Sampling standard uncertainty: $u_{sampling}$ (mg/kg)	3,6
Relative sampling uncertainty: $u\%_{sampling}$ (%)	**4,0**
Measurement standard uncertainty: u_{meas} (mg/kg)	4,2
Sampling uncertainty vs. the measurement uncertainty $u\%_{\mathbf{s/meas}}$ (%)	**76**

Sampling uncertainty
by element and device



In conclusion (1)

- The sampling contribution due to different sampling devices/techniques is calculated
- It represents the repeatibility of sampling operations;
- No bias (systematic) effects are considered both for sampling and analysis;
- The sample preparation is included in sampling uncertainty (from primary sample to test sample) and in the analytical uncertainty (from test sample to test portion

In conclusion (2)

- The sampling uncertainty calculated is site-specific and is applicable:
  - to analogue soil situation and similar range of mass fractions;
  - To new independent measurements of soil collected in the same area.
- Sampling within the site can be the dominant component of the measurement uncertainty (typical in most environmental matrix);
- The spatial variation component is erased in the calculation considering only the nugget.