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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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 \( m(x) \))
- \( \varepsilon \) = uncorrelated random noise
- \( x \) = location
Geostatistics (2)

Geostatistical analysis include two phases:

- spatial modelling (variography);
- spatial interpolation (kriging)
The Experimental Variogram

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

- **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

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

\[ s_{\text{tot}}^2 = s_{S}^2 + s_{T}^2 + s_{A}^2 + s_{SP}^2 \]

- \( s_{\text{tot}}^2 \) comprises:
  - the variances of sampling \( s_{S}^2 \),
  - sample treatment/reduction \( s_{T}^2 \),
  - analysis \( s_{A}^2 \),
  - and the spatial variability \( s_{SP}^2 \)

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:

\[ u_{\text{sampling}} = \sqrt{s^2_{\text{sampling}}} \]

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

\[ u\%_{\text{sampling}} = (u_{\text{sampling}} / x_{\text{mean}}) \times 100 \]

The **sampling expanded uncertainty** is:

\[ U_{\text{sampling}} = ku_{\text{sampling}} \quad (k = 2) \]
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 $u_{s\text{ampling}}$, 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

Data set of 105 values for each device
Hand auger

Mechanical auger

Shovel
Variogram parameters

Directional Variogram (90°) - Zinc (mg/kg) - Auger

Objective = 1365.085
Calculation (1)

\[ s^2_{\text{sampling}} = s^2_{\text{nugget}} - (s^2_{\text{analysis}} + s^2_{\text{sample reduction}}) = 17.3 - 4.1 = 13.2 \]

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

Were calculated together experimentally analysing 10 replicates (test portions) taken from 3 independent test samples
The sampling standard uncertainty is:

\[ U_{\text{sampling}} = \sqrt{S^2_{\text{sampling}}} = \sqrt{13.2} = 3.6 \text{ mg/kg} \]

As uncertainty relative to the Zn mean concentration (90.2 mg/kg) becomes:

\[ U_{\% \text{ sampling}} = \left( \frac{3.6}{90.2} \right) \times 100 = 4 \% \]

The sampling expanded uncertainty is:

\[ U_{\text{sampling}} = k \times 3.6 = 7.3 \text{ mg/kg} \ (k = 2) \]
Measurement standard uncertainty (from nugget value)
\[ u_{\text{meas}} = 4.2 \text{ mg/kg} \]

Sampling uncertainty (subtracting analytical uncertainty from measurement uncertainty)
\[ u_{\text{sampling}} = 3.6 \text{ mg/kg} \]

The contribution of the sampling to the measurement uncertainty is:
\[ u_{\% s/meas} = \left( \frac{3.6}{4.2} \right) \times 100 = 76 \% \]
### Uncertainty budget

<table>
<thead>
<tr>
<th></th>
<th>Zinc</th>
<th>Auger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element mean value</td>
<td>$x_{\text{mean}}$ (mg kg$^{-1}$)</td>
<td>90,2</td>
</tr>
<tr>
<td>Nugget variance</td>
<td>$s_{\text{nugget}}^2$</td>
<td>17,3</td>
</tr>
<tr>
<td>Analytical variance</td>
<td>$s_{\text{analytical}}^2$</td>
<td>4,1</td>
</tr>
<tr>
<td>Sampling variance</td>
<td>$s_{\text{sampling}}^2$</td>
<td>13,2</td>
</tr>
<tr>
<td>Sampling standard</td>
<td>$u_{\text{sampling}}$ (mg/kg)</td>
<td>3,6</td>
</tr>
<tr>
<td>Relative sampling</td>
<td>$u_{%\text{sampling}}$ (%)</td>
<td><strong>4,0</strong></td>
</tr>
<tr>
<td>Measurement standard</td>
<td>$u_{\text{meas}}$ (mg/kg)</td>
<td>4,2</td>
</tr>
<tr>
<td>Sampling uncertainty</td>
<td>vs. the measurement</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>uncertainty</td>
<td></td>
</tr>
<tr>
<td>$u_{%\text{s/meas}}$ (%)</td>
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<td></td>
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</tbody>
</table>
Sampling uncertainty by element and device

Uncertainty of Sampling

<table>
<thead>
<tr>
<th>element</th>
<th>Auger</th>
<th>Mech. Auger</th>
<th>Shovel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<tr>
<td>Cr</td>
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</tbody>
</table>

u % sampling
In conclusion (1)

- The sampling contribution due to different sampling devices/techniques is calculated.
- It represents the repeatability 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.