**University of Stuttgart**
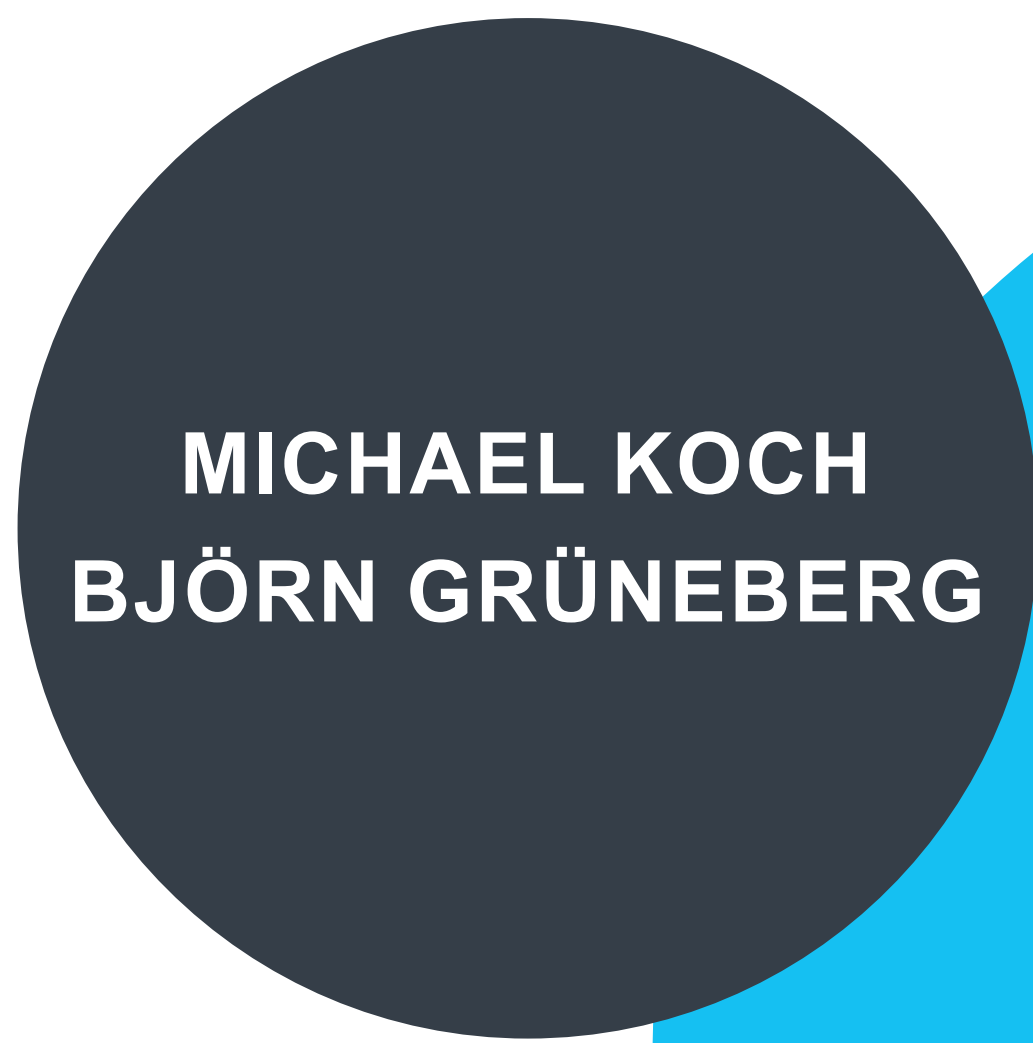Germany
AQS Baden-Württemberg
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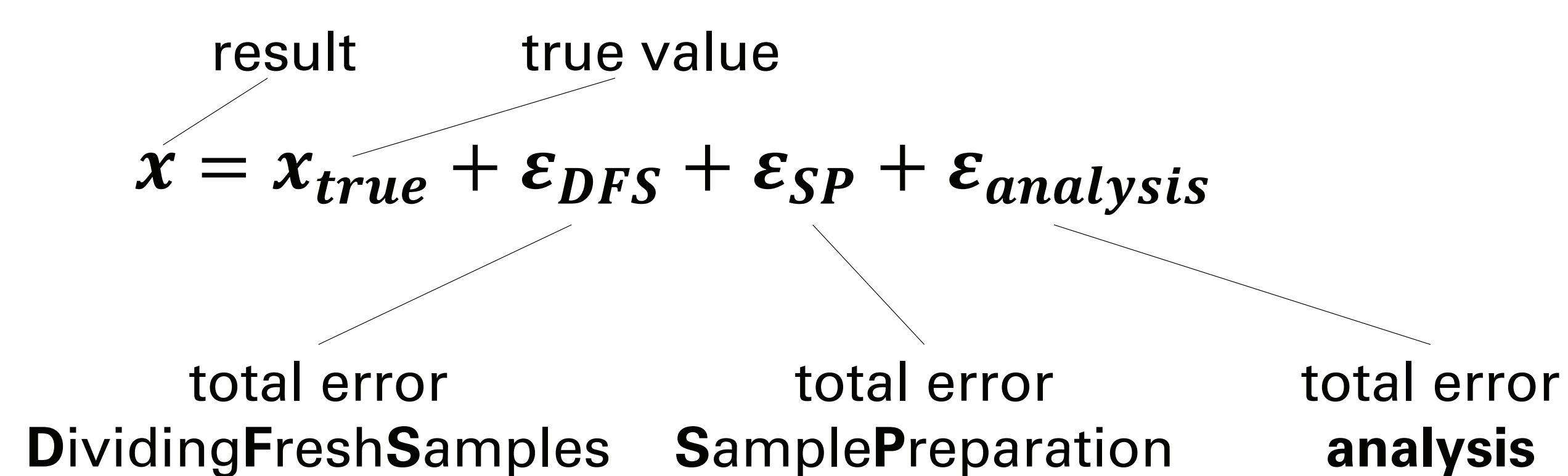# Proficiency test for sample preparation in soil analysis

## Introduction

A proficiency test (PT) for the preparation of soil samples for analysis of dry residue, loss on ignition, ammonium-N and nitrate-N in CaCl$_2$-extract, pH, electrical conductivity, total carbon and total nitrogen was organised by Berlin-Brandenburg State Laboratory (LLBB).

For the evaluation ANOVA is used to separate the contributions of sample pretreatment (homogenization and division of fresh samples), sample preparation (drying, sieving, dividing, grinding) and analysis.

- sample pretreatment     made by PT provider
- sample preparation     made by participants
- analysis     made by participants

## Statistical model

$$x = x_{true} + \varepsilon_{DFS} + \varepsilon_{SP} + \varepsilon_{analysis}$$

result    true value

total error **D**ividing**F**resh**S**amples    total error **S**ample**P**reparation    total error **analysis**

## ANOVA

$$s^2_{total} = s^2_{DFS} + s^2_{SP} + s^2_{analysis}$$

Since no quantity is measured without sample preparation only the sum of variances from DFS and SP can be estimated

$$(s^2_{DFS} + s^2_{SP}) = s^2_{total} - s^2_{analysis}$$

Variance of analysis is calculated from the mean of variances of triplicate analyses (standard deviations from Q method), the total variance from all data using also the robust method

## Sample pretreatment

Coarse sieving (approx. 5 mm), mechanical homogenization and dividing



| Sample preparation | analysis |
|---|---|
| **Homogenise** - intensive rolling, stirring, pouring over, etc. in the bag before opening | **Dry residue** at 105 °C<br>**NH$_4$-N and NO$_3$-N** in CaCl$_2$ extract |
| **Drying** at max. 40 °C<br>**Sieving** to < 2 mm<br>**Dividing** into 3 measuring samples<br>send back prepared samples to provider | **Dry residue**<br>**Loss on ignition**<br>**pH value** in 0.01 M CaCl$_2$<br>**Electrical conductivity** |
| **Grinding** to < 250 µm<br>send back prepared samples to provider | **Total carbon**<br>**Total nitrogen** |



## Proficiency assessment

**Standard deviation from dividing fresh samples $s_{DFS}$** estimated from measurement results of PT provider:

$$s_{DFS} \leq 0.5 - 2.0\ \%$$

**Assessment of sample preparation and analysis using z' score:**

$$z' = \frac{x_i - x_{pt}}{\sqrt{s^2_R + s^2_{DFS}}}$$
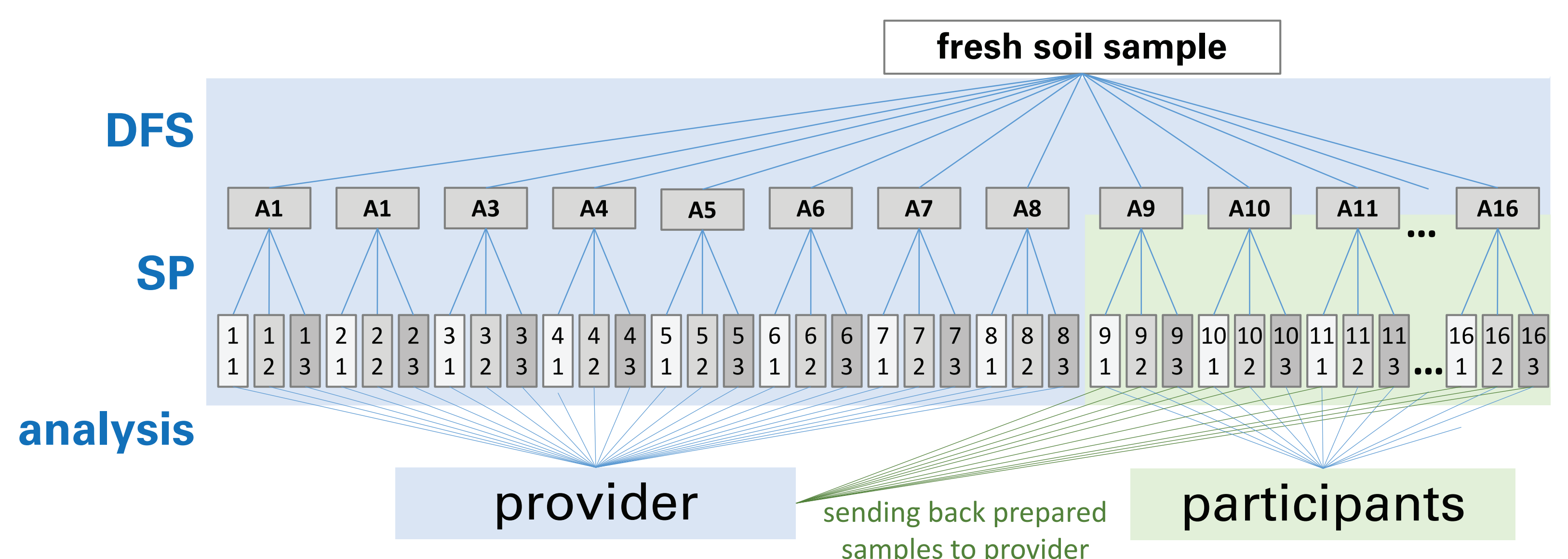
**Assessment only for sample preparation**

$$z' = \frac{x_i - x_{pt}}{\sqrt{s^2_R + s^2_{DFS} + s^2_{analysis}}}$$

## Outcome of the PT

Uncertainty contribution from fresh sample division (DFS) + sample preparation (SP) is low, e.g. compared to usual measurement uncertainties.
Uncertainty contribution of the SP after deduction of the DFS:

$$s_{SP} < 2.5\ \%$$

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