Symposium BAM 15. April 08

Measurement Uncertainty for Cd and P in Agricultural Top Soil

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Evaluation:

1. Modelling approach (single effect investigation, ISO/DIN "GUM")

2. Laboratory validation approach (process replication, ISO/DIN 5725)

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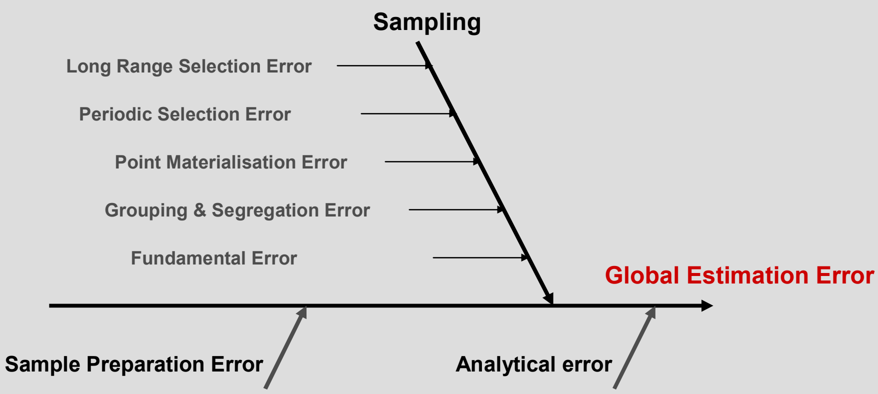
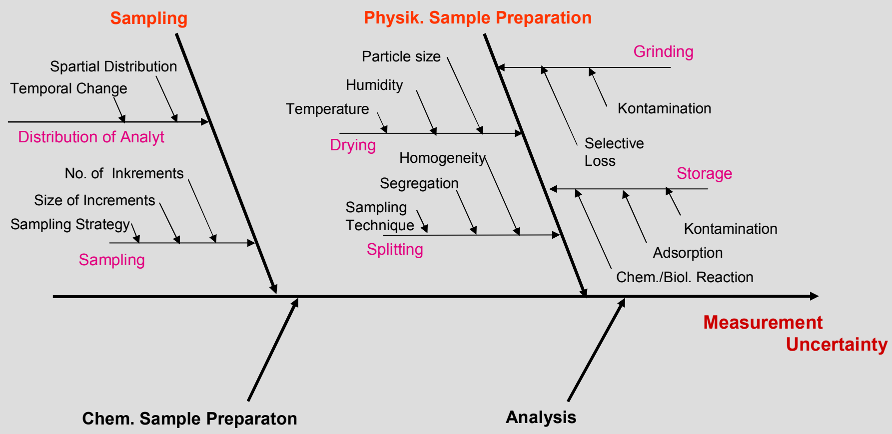
Modelling Approach

Classification of Effects in Sampling

("Sampling Theory" according to **Gy**)

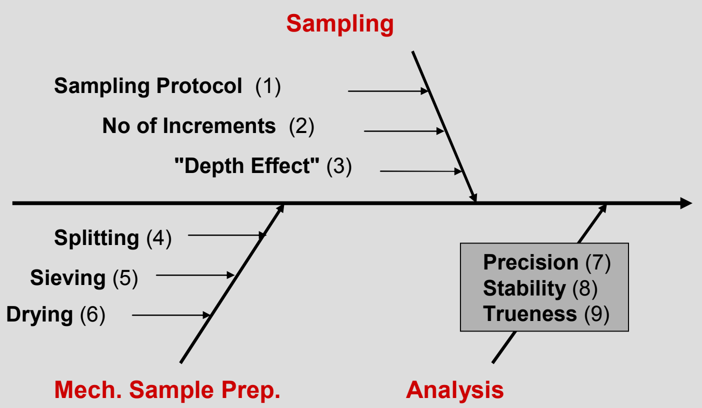


Effects in Soil Sampling



Modelling - Case Study

Tested Effects in Sampling, Sample Preparation and Analysis



Case Study

0.315 ha (143 m x 22 m)

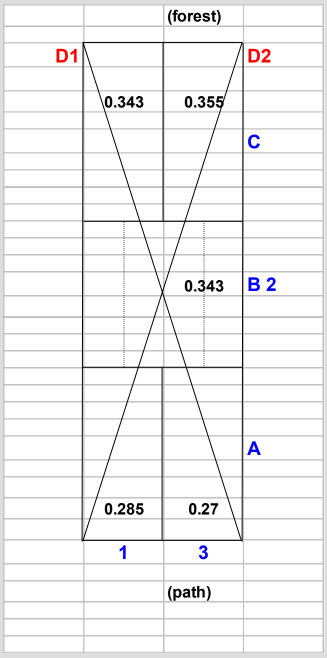
Definition of measurand:

- Mass fraction of analyts of a soil body of 30 cm depth
- Sample material air dryed, ground, and sieved to < 2 mm
- Sample produced according to a specified sampling protocol

Sampling Protocol (Strategy):

- Sampling scheme: Diagonal
- Auger sampling device
- 20 increments per ha

Modelling Approach



1. **Sampling Strategy** (system. effect)

Reference-Sampling:

5 composite samples from squares A1, A3, B2, C1, C3; 18 incr. each

Difference **D1** and **D2**

(Cd) $\Delta x_{Diag} = 2.8\ \%$

("Typ B": U-Distribution) $u_{Prot} = \frac{\Delta x_{Diag}/2}{\sqrt{2}}$

$u_{Prot} = 1.0\ \%$

Modelling Approach

2. Between Increment Locations
(random effect)

9 increments on square B
(10 m x 10 m)

Increment	x (mg/kg)
1	0.364
2	0.411
3	0.468
4	0.413
5	0.370
6	0.376
7	0.389
8	0.376
9	0.464
s_{ws} = 9.8 %	

(Cd)

Long range heterogeneity (betw. sqr): s_{bs} = 12 %

Short range heterogeneity (within sqr): s_{ws} = 9.8 %

$$s_{Incr} = \sqrt{s_{bs}^2 + s_{ws}^2} = 16\ \%$$

("Typ A":
Normal Distribution)

$$u_{Incr} = \frac{s_{Incr}}{\sqrt{n_{Incr}}}$$

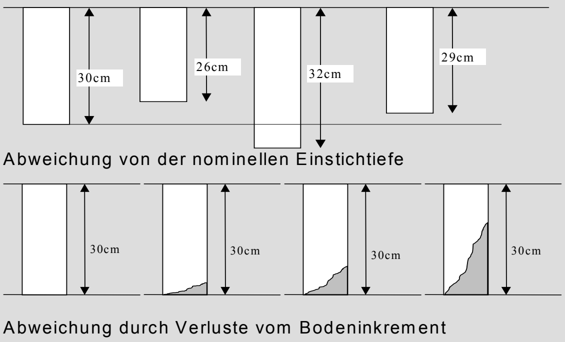
(each diagonal: n_{incr} = 9)

u_{Incr} = 5.4 %

Modelling Approach

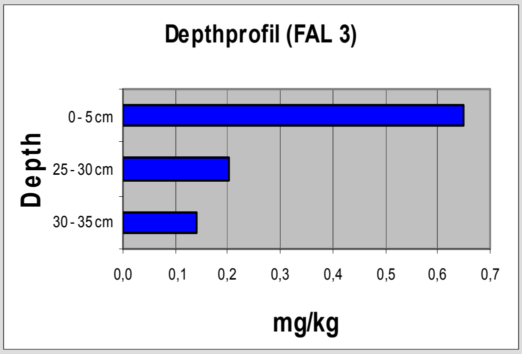
3. Depth Effect (1)

"Materialisation error"
(Delimination and Extraction)



3. Depth Effect (2)

Analyt gradient in depth



Analytical values of cores
(mean of 5 cores):

(Cd)

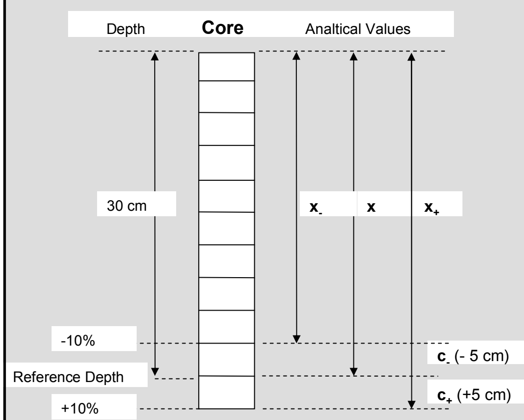
(Ref. Depth)
– 5 cm: $c_- = 0.14$ mg/kg

(Ref. Depth)
+ 5 cm: $c_+ = 0.10$ mg/kg

3. Depth Effect (3)

Transformation

Difference in depth ⇒ Difference in analyte content

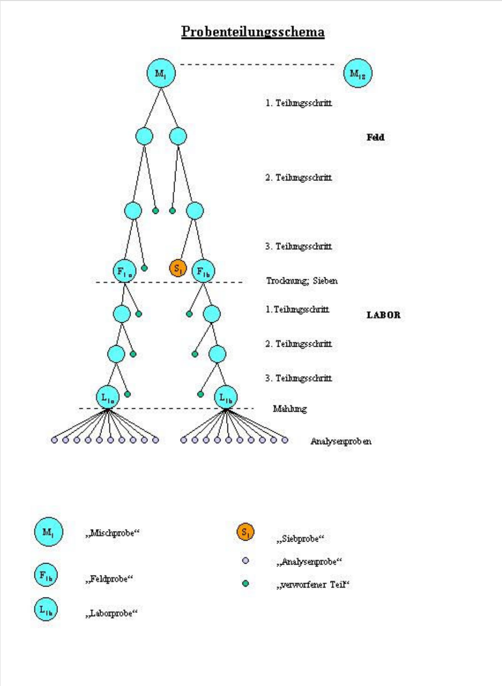


Assumption:
max. deviation from ref. depth: ± 10%

("Type B": Triangle Distribution)

$$u_{Depth} = \frac{(x_+ - x_-)/2}{\sqrt{6}}$$

(Cd) u_{Depth} = 3.5 %

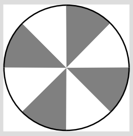


Modelling Approach

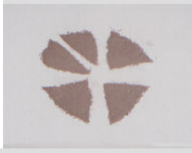
4. Sample Splitting (1)

Test of duplicates
from field samples (n = 18)

Method:
„pizza pieces“: 6 times to half mass



rejected
mixed again

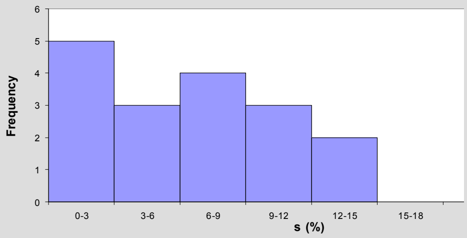


Modelling Approach

4. Sample Splitting (2)

("Typ A":
Normal Distribution) $u_{Split} = s_{Split}$

Distribution of standard deviations
from 18 duplicate measurements



(Cd)

Mean of standard deviations: $s_{Split} = 5.0\%$

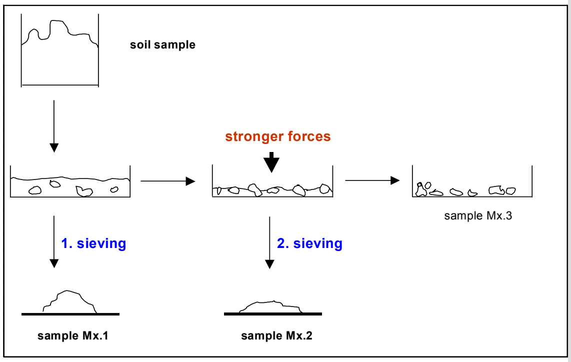
$u_{Split} = 5.0\%$

5. Sieving (particle size < 2mm)

Test of field samples (n = 6)

Max. difference Δ_{Siev} in analyte content of samples after 1. sieving (low force) and 2. sieving (stronger forces)

$$\Delta_{Siev} = | c_{1.s} - c_{2.s} |$$



(Cd) $\Delta_{Siev} = 6.6\ \%$

("Type B" Rectangular distribution)

$$u_{Siev} = \frac{\Delta_{Siev}/2}{\sqrt{3}}$$

$$u_{Siev} = 1.9\ \%$$

Modelling Approach

6. Drying

Water content in prepared analytical samples

Reference *:

For a large number of sieved and *air dried* soil samples a water content was found between 1 - 3 %.

* R. Dahinden, A. Desaules
Die Vergleichbarkeit von Schwermetallanalysen in Bodenproben von Dauerbeobachtungsflächen
Eidg. Forschungsanstalt für Agrikulturchemie und Umwelthygiene, Bern 1994

$\Delta_{Dry} = 2.0\ \%$

("Type B" Rectangular distribution)

$$u_{Dry} = \frac{\Delta_{Dry}/2}{\sqrt{3}}$$

$$u_{Dry} = 0.6\ \%$$

Instrumental Analysis

Single laboratory validation data

Analytical Methode

Cd: Solid Sampling Zeeman-Graphitfurnace-AAS

	Uncertainty contribution	***Evaluation***	***Standard-uncertainty***
7.	Repeatability	Precision of test samples ("Typ A" Normal Distribution)	u_{rw} = 3.6 %
8.	Long-term Stability	Control chart ("Typ A" Normal Distribution)	u_{bias} = 2.7 %
9.	Trueness	Cert. Referencematerial (CRM) ("Typ B" Normal Distribution)	u_{ref} = 2.7 %
	Combined analytical uncertainty		u_{anly} = 5.2 %

Uncertainty - Budget

Estimation of **Combined Measurement Uncertainty**

			Standarduncertainty Cd	**P**
1.	Sampling protocol	Sampling	1.0 %	0.5 %
2.	Between locations		5.4 %	2.9 %
3.	Depth effect		3.5 %	3.7 %
4.	Splitting	Sample Prep.	5.0 %	2.5 %
5.	Sieving		1.9 %	2.4 %
6.	Drying		0.6 %	0.6 %
7.	Repeatability	Inst. Analysis	3.6 %	0.6 %
8.	Stability (lab. bias)		2.7 %	-
9.	Trueness		2.7 % [1]	9.7 % [2]
	Combined Uncertainty		**9.1 %**	**11.3 %**

[1] Confidence interval of CRM BCR 280

[2] S_R from an Inter-Laboratory Comparison

Laboratory Validation Approach

Six independent sampling processes

- Sampling under reproducibility conditions
- Analysis under repeatabiliy conditions

Sampler	Diagonal	Cd (mg/kg)
1	D1	0.314
2	D1	0.304
3	D1	0.345
4	D2	0.313
5	D2	0.313
6	D2	0.350

$\bar{x}$ = 0.323

s_R = 6.0 %

Samp = R

Measurement Uncertainty
(including the analytical components u_{bias}, u_{ref}):

u_{meas} = **8.0 %**

Case Study

Measurement Uncertainty for Cd and P in Agricultural Top Soil

Comparison of Methods

Expanded Uncertainty : $U_{meas} = k \times u_{meas}$

	Laboratory Validation	Modelling
Cd	**19 %** 1)	**18 %** 3)
P	**26 %** 2)	**23 %** 4)

Faktor k for approx. 95% coverage:
1) k = 2.4 (df_{eff} = 7)
2) k = 2.1 (df_{eff} = 20)
3) k = 2.0 (df_{eff} > 30)
4) k = 2.0 (df_{eff} > 30)

Report "PronAck"

Ulrich Kurfürst et al.:

**Repräsentanz von Probennahmeverfahren auf Ackerflächen
- eine Fallstudie zur Ermittlung der Messunsicherheit für Cadmium und Phosphor
(Endbericht)**

**Representativity of Sampling on Arable Land
- a Case Study of Evaluation of Uncertainty in Measurement for Cadmium and Phosphorus
(Final Report)**

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