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Adequate data quality: Essential methodological soil monitoring challenge

André Desaules and Stefan Ammann
andre.desaules@art.admin.ch

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Observatoire national des sols
Osservatorio nazionale dei suoli
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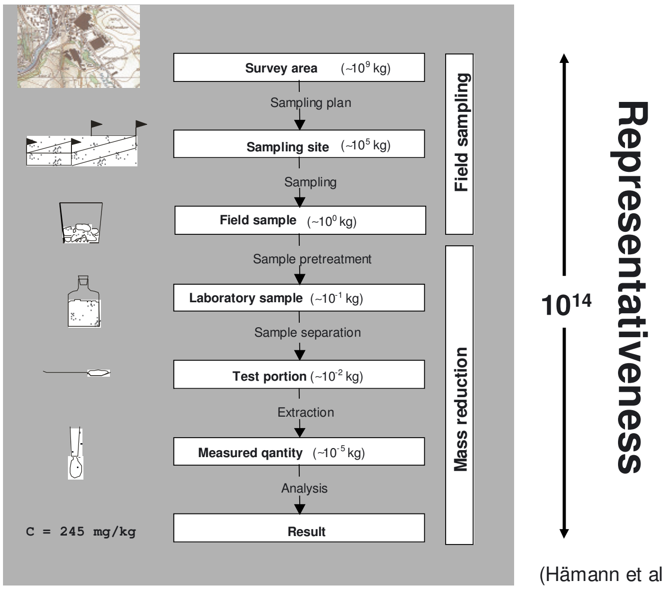
From the presentation on „Advances in soil monitoring“ it became obvious that the continuous quantitative control of data quality is an essential soil monitoring challenge besides the control of other relevant boundary conditions.

Outline

- Fundamentals of data quality
- Temporal measurement stability: Monitoring requirement
  - Analytical ‘stability’
  - Soil sample ‘stability’
  - Methodology to ‘stabilize’ analytical time series
  - Soil sampling ‘stability’
  - Measurement time series ‘stability’
- Measurement comparability: Status and reference requirement
- References

Problem - Objective - Challenge



(Hämann et al. 2003)

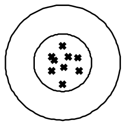
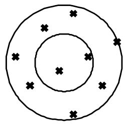
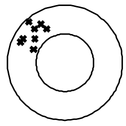
Problem: Heterogeneity of particluar material as soil.

Objective: Sampling of representative soil samples and subsamples along the whole measurement chain.

Challenge: To grant for the sample representativity over 14 orders of magnitude!

Note: Most sampling steps (mass reduction and subsampling) are performed in the laboratory.

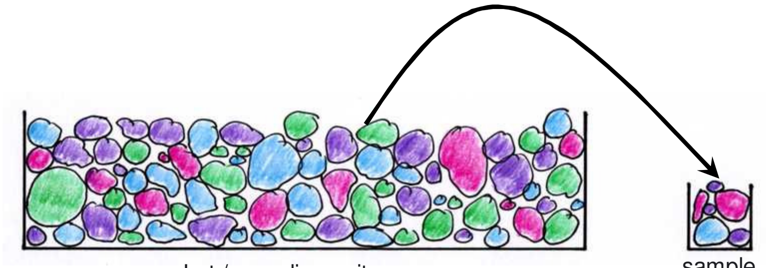
Terminology and relationships

Error type::		Random error	Systematic error (bias)
			
Precision:	good	poor	very good
Accurracy:	very good	good	poor
Correctness:	yes	no	no

Measurement stability: „The gun and the target are fix over time“ (Desaules et al. 2000)

According to Pierre Gy‘s sampling theory and practice (promoted by EPA), measurements which are performed in a correct way are always precise, accurate and reproducible in theory. In practice ,however, errors are unavoidable and must be minimized as much as possible and quantified to be accounted for.

Pierre Gy‘s sampling theory: (1) Fundamental error FE



- Constitution heterogeneity CH
- Distribution heterogeneity DH
- DH </= CH

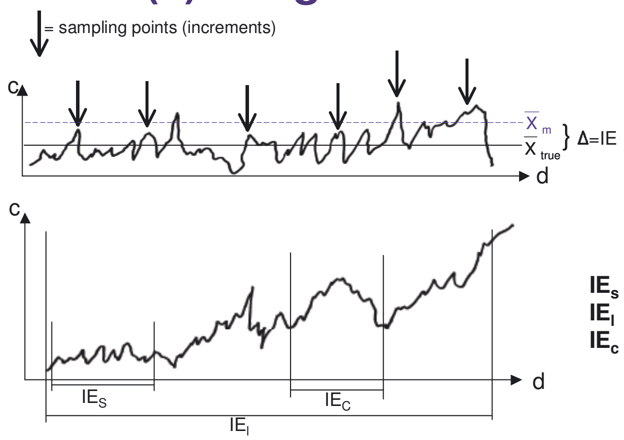
FE only error which is never 0

> increasing of sample
> comminution (grinding) *before* (sub)sampling

Sampling errors occur, if the **proportionality** between the sampling unit and the sample is not given, then the sample is **not representative.**
According to Pierrre Gy there are 5 different types of sampling errors which are illustrated as follows with indications to reduce them:

(1) The fundamental error is the only one which can never be 0 in heterogeneus material. It can be reduced by increasing the sample and/or to grind the material **before** (sub)sampling.

(2) Integration error IE



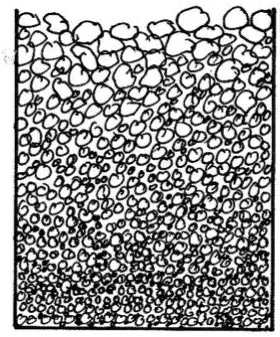
IE$_s$ short-range
IE$_l$ long-range (trend)
IE$_c$ cyclic

- **as many increments as possible**
- **increasing sampling support (smoothing)**
- **variographic sampling (preliminary investigation)**

(Pitard 1993)

(2) Integration error: only if the material of the whole sampling unit would be extracted and reduced correctly, the measured mean value would be equal to the true mean value. There are 3 error reduction possiblilities.

(3) Grouping and segregation error GE



GE = DH
Cause: gravity

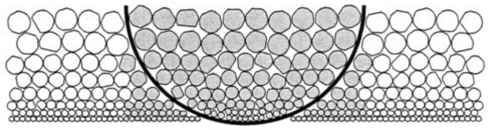
> As many probabilistic increments as possible

> Mixing (valuable for very short-terme only)

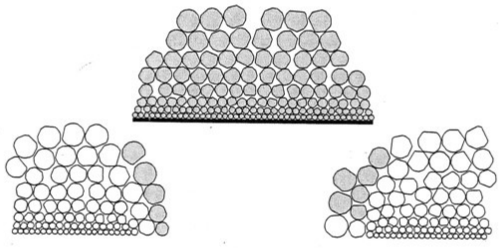
(3) Grouping- and segregation error: Under gravity conditions heterogeneus material inevitably segregates.

(4) Materialization error ME

ME = DE + EE



(4a) Delimitation error DE)



(4b) Extraction error EE

> best adapted devices (no standardisation) (Pitard 1993)

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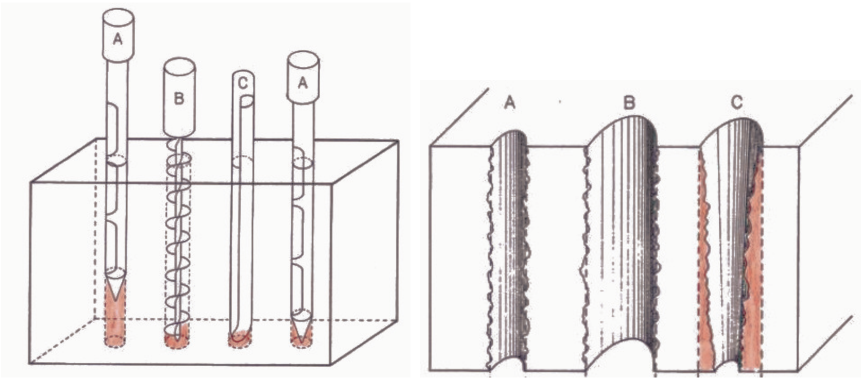
(4) The materialization error is composed by the delimitation- and the extraction errors (all grey pebbles would belong to the correct sample.

Delimitation errors by sample devices



(Pitard 1993)

The main problem of a correct sample delimitation is at the basis.

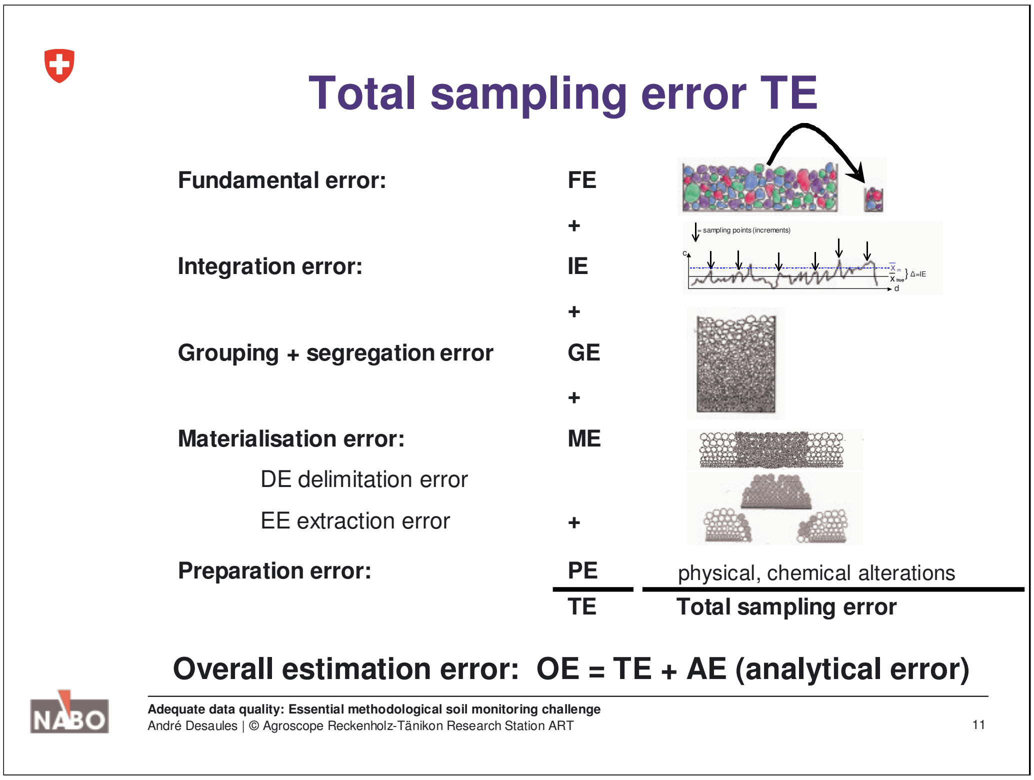
(5) Sample preparation error PE

Concerns all operations which (selectively) alter the sample in A relevant way:

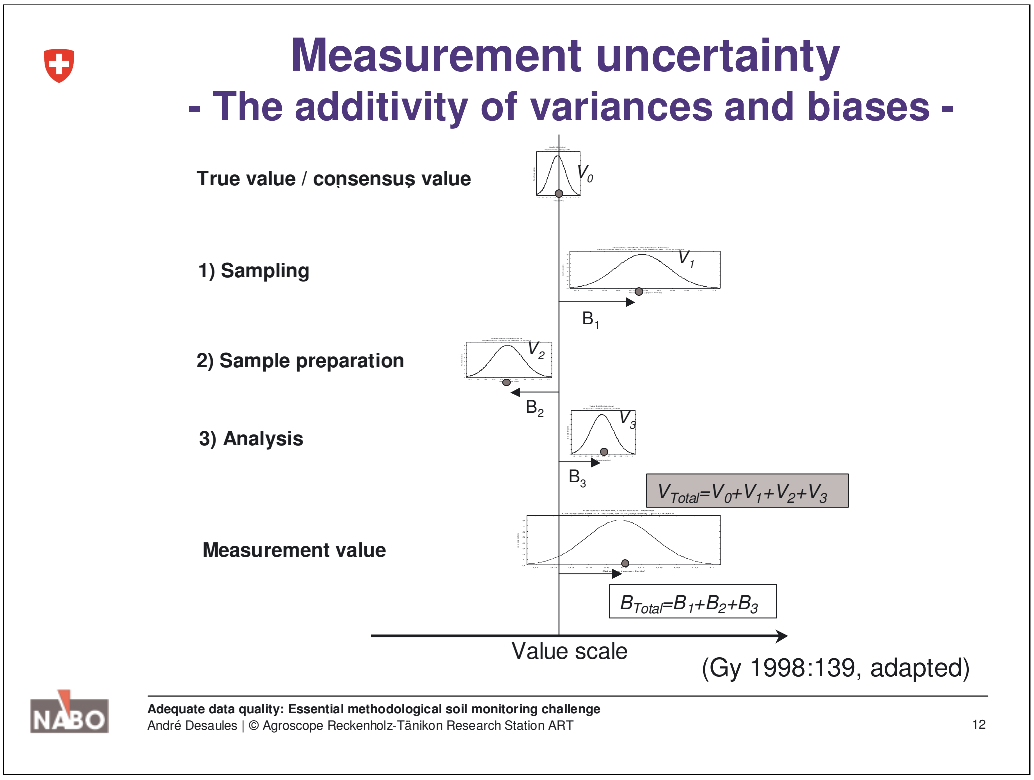
- **Contamination**
- **Dilution**
- **Loss (selective)**
- **Physical alteration**
- **Chemical alteration**

> Qualified manpower

(5) The sample preparation is part of the sampling process, because it may alter the proportionality of the samples in a qualitative or quantitative way.



Summary of the total sampling error and the overall estimation error including the analytical error.



In the current practice measurement uncertainty is still often only adressed by variances (frequently only by analytical precision) and the other error components are neglected, especially bias which is generally much more important but also much harder to quantify. This is an important source of misinterpretation.

Reliable quantitative informations of the whole measurement uncertainty from sampling to chemical analysis is crucial for correct interpretations but very rare in scientific practice!!!

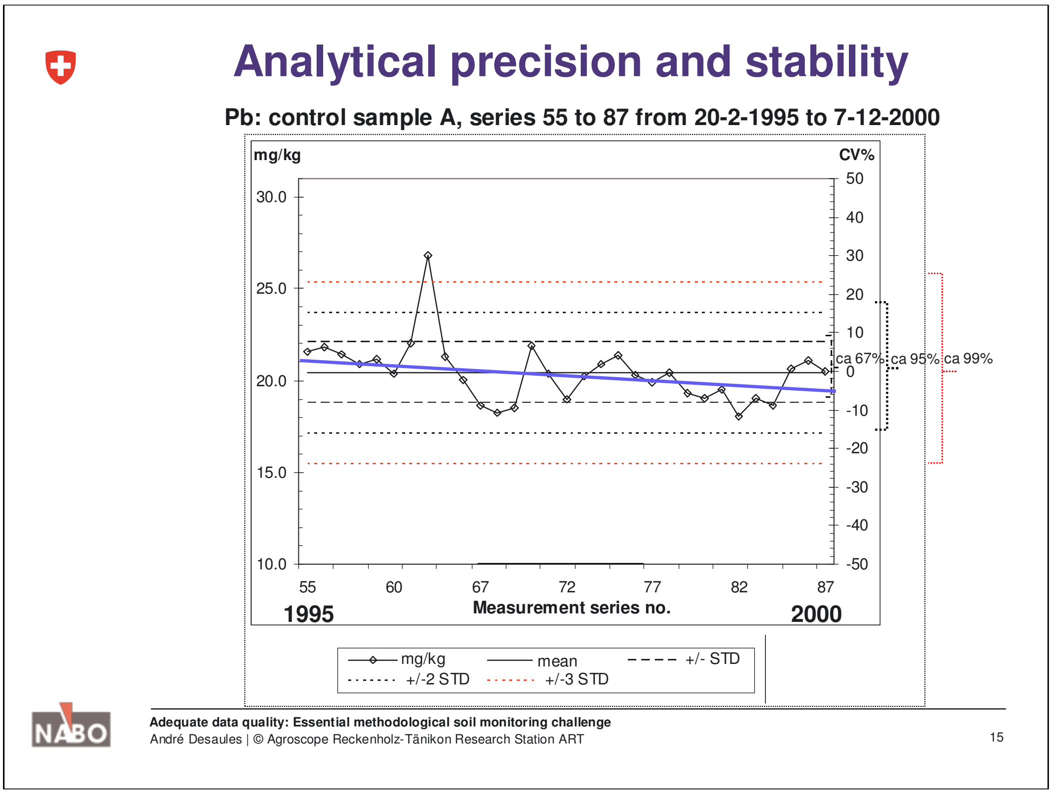
Definition of adequate data quality in chemical soil monitoring

Best possible performances of the three following data quality parameters with continuous quantitative control over the whole measurement chain:

- Measurement precision: sensitivity to detect soil changes
- Measurement stability: baseline reference for soil changes
- Measurement comparability and accuracy: reference for other studies

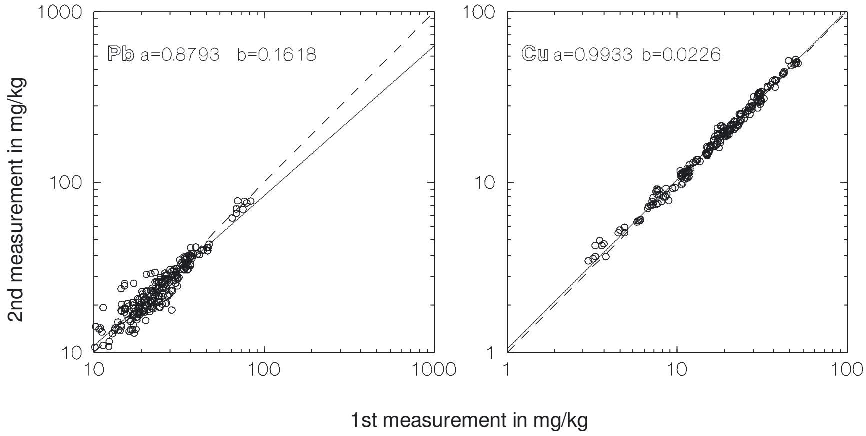
Temporal measurement stability:

Monitoring requirement



The control chart for Pb over 5 years shows an analytical precision of +/- 8% CV and an apparent negative drift. What is unstable: the measurement system or the sample? Analytical between series bias (new standard, new detection method) was one of the most important identified temporal bias component.

Soil sample stability (1)

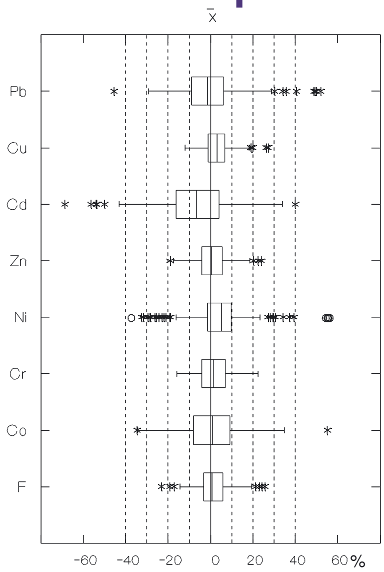


Deviations of the 2nd measurements after five years (n = 227)

(Desaules et al. 1996)

On the loglog graph of Cu shows a perfect agreement, and that of Pb a negative bias.

Soil sample stability (2)

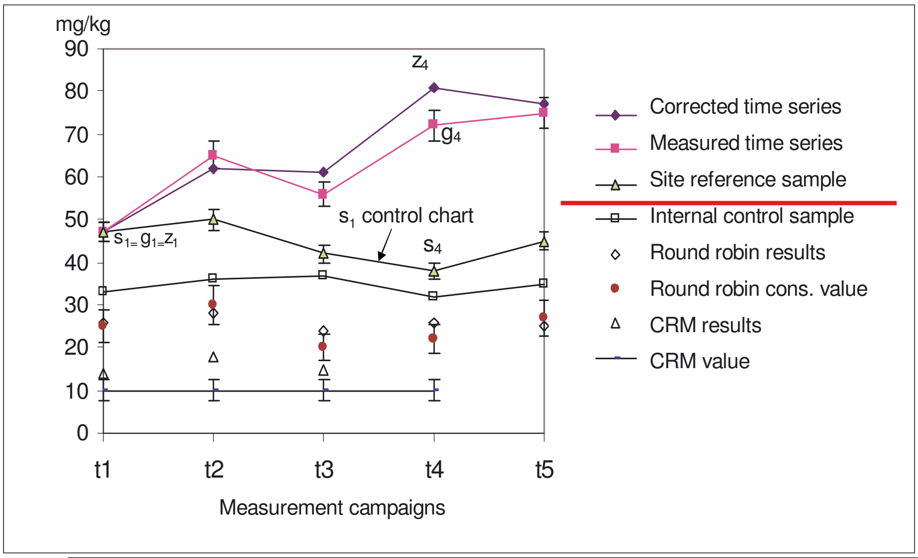


Deviations of the 2nd measurement after five years from the mean of both measurements (n = 227)

(Desaules et al. 1996)

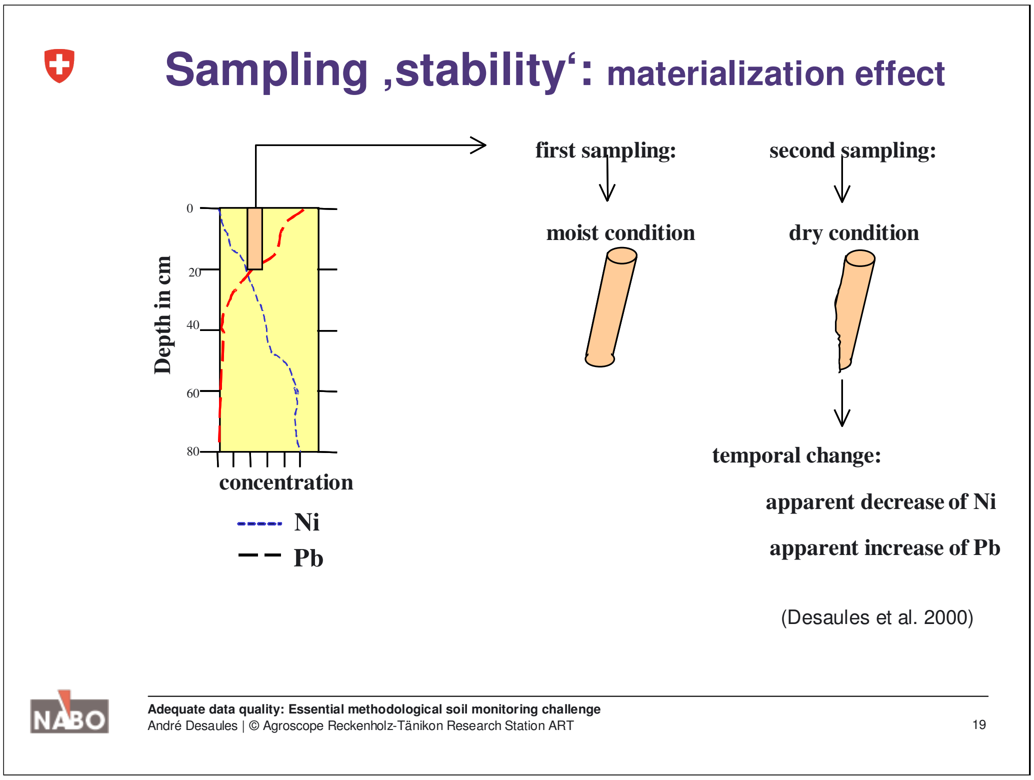
On the basis of the deviation of the mean of both measurements the negative mean bias of Pb is confirmed while Cu shows a positive mean bias. Cd shows the worst reproducibility but no data were available for Hg.

Methodology to ‚stabilize‘ analytical time series

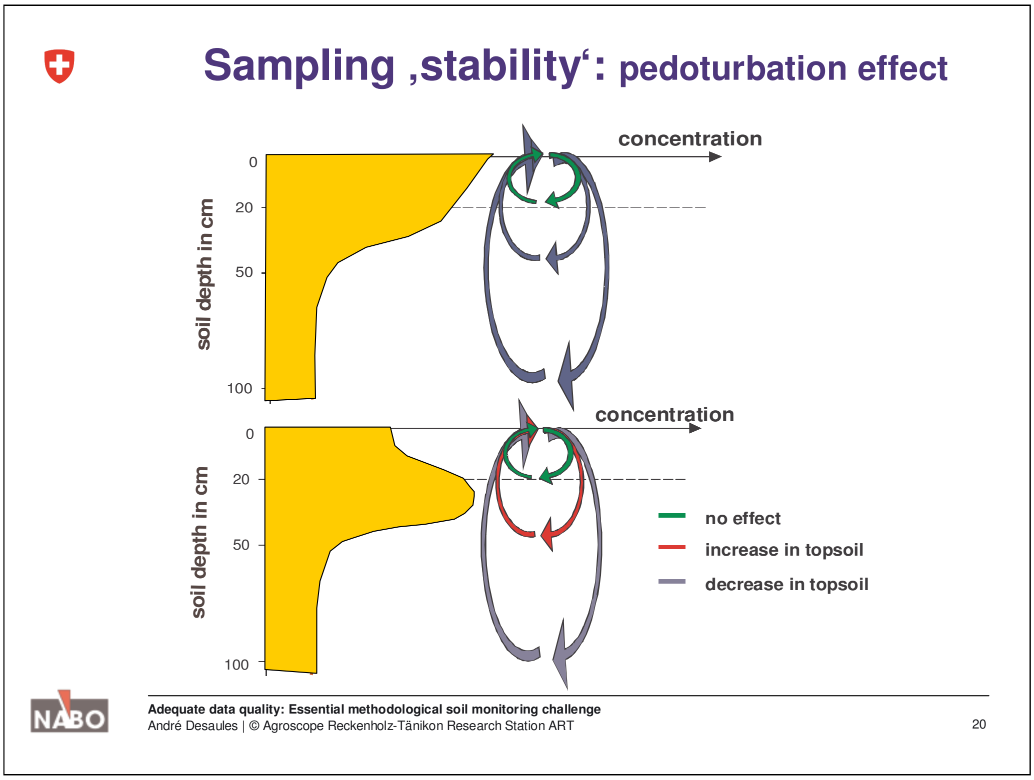


The measured time series (mean of n = 4) at each site is corrected by the parallel measurements of the site reference samples (samples of the 1st campaign = control chart of s_1 samples)

The best quantitative control system is as close as possible to the matrix and concentration levels of the individual soil monitoring sites.

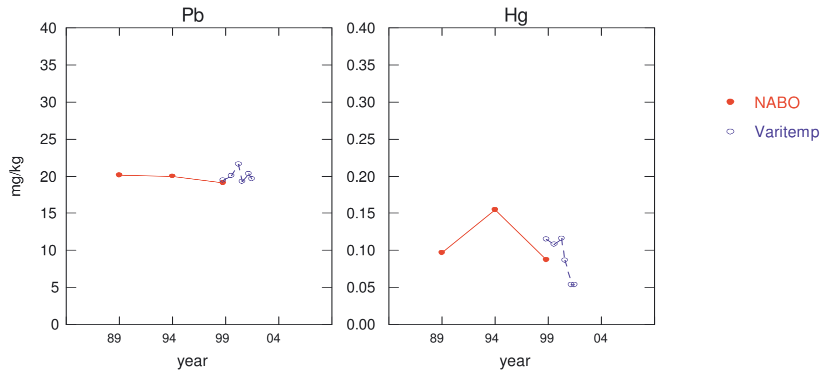


Selective differences in sample materialization at different concentration gadients lead to apparent changes (artefacts) > comparison of apples with pears.



Changes due to various pedoturbation depth and concentration gradients.

Measurement time series ‚stability‘



Permanent grassland, sampling depth 0-20cm

(Desaules et al. 2004)

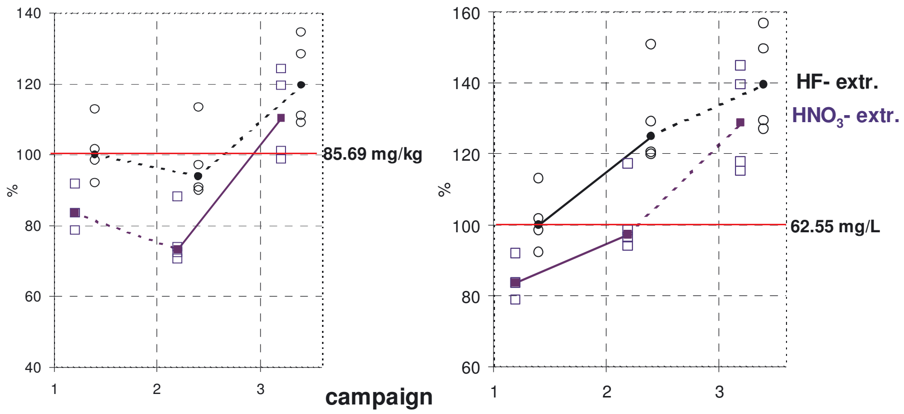
Comparison of the NABO time series of 10 years with 3 measurements (red), and the Varitemp time series of 3 years with 6 measurements (blue).

Observation: The effect of the periodicity is greater than the length of the time series. Conclusion: **time series measurements in soils without artefacts are not yet feasible!**

Mass to volume conversion:

Bulk density effect

Pb: Novaggio, beech forest



Bulk density (kg/L): 0.73 0.97 0.85

(Desaules, Baize et al. 2004)

The evolution of changes is different on mass- or volume basis, affected by changes of bulk density (Sampling depth effect?).

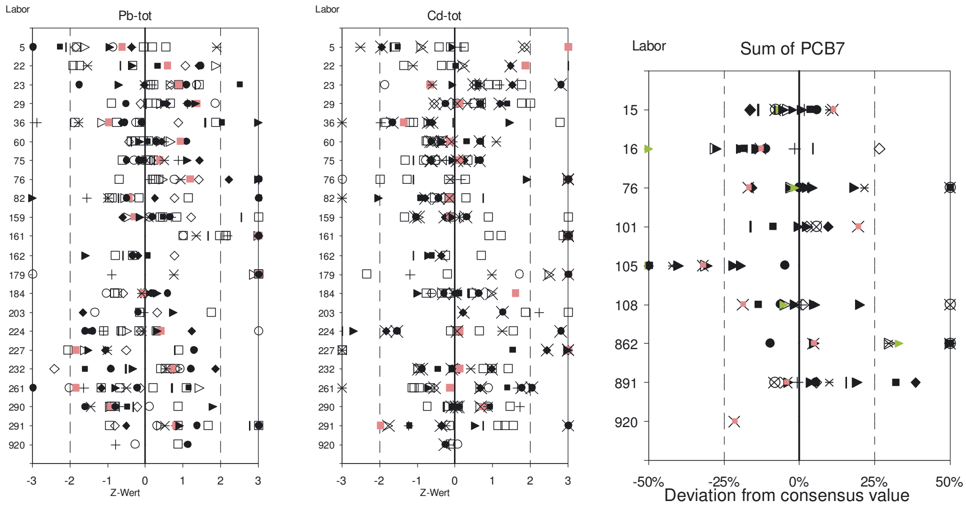
Conclusion: Further soil characteristics should continuously be analyzed for sake of sample comparability.

(Additional observations: The temporal comparison between 2 chemical analysis methods are fairly parallel)

Measurement comparability:

Status requirement

Analytical round robin (2007)

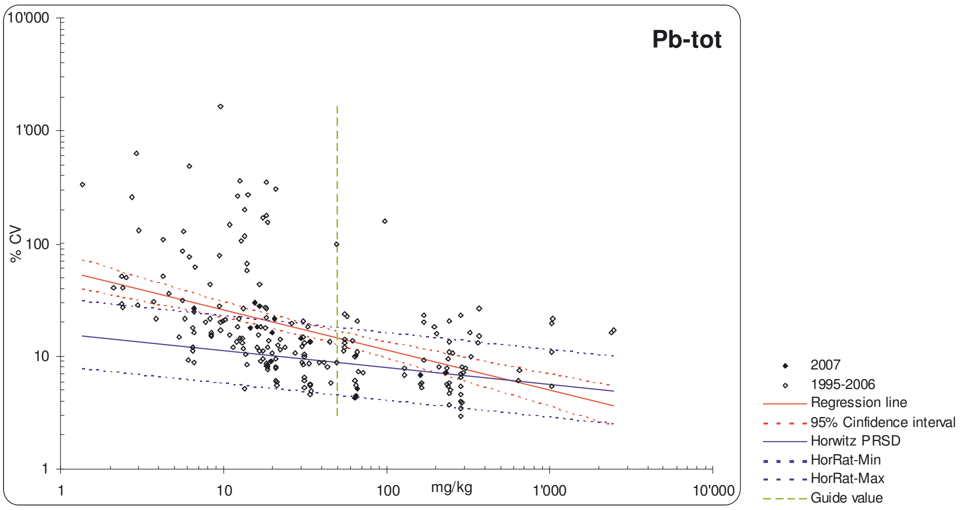


Deviations from mean values (consensus values)

(Ammann et al. 2008)

Annual round robin programme since 1989 in collaboration with Wageningen Evaluation Programs for Analytical Laboratories WEPAL in the Netherlands (www.wepal.nl). 12 samples per year, to approach routine conditions.

Analytical variation as function of concentration: Pb



(Ammann et al. 2008)

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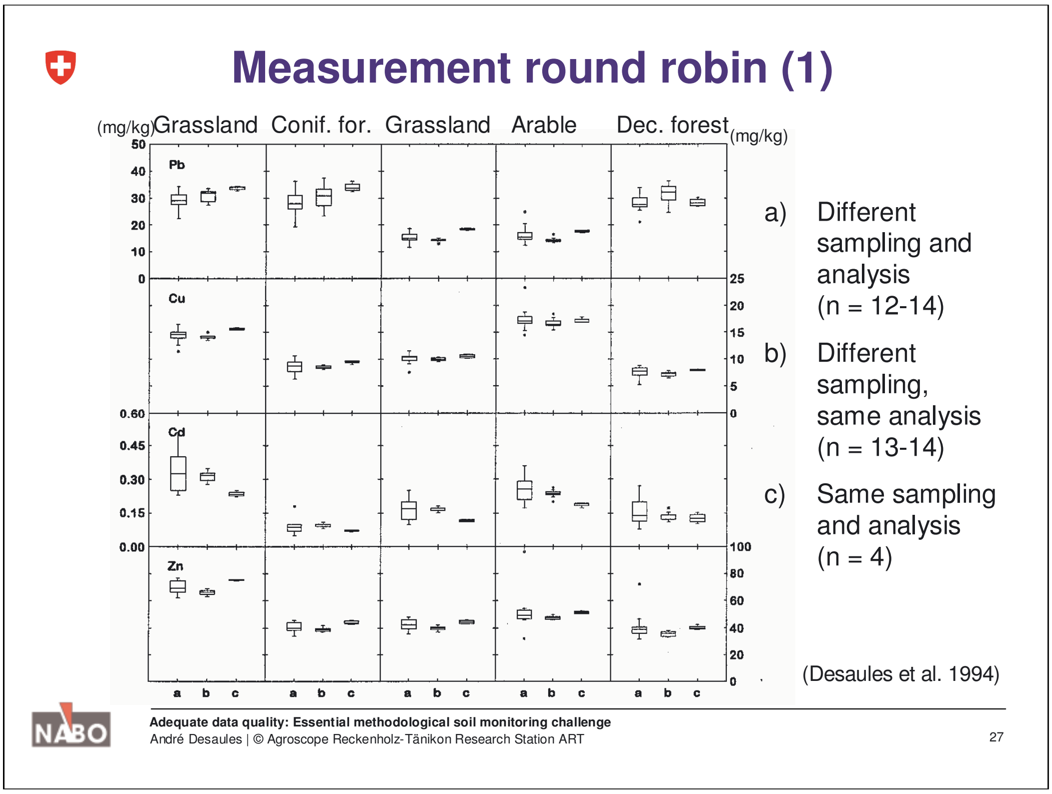
Round robin performance 1995 to 2007 (red regression line) compared to the Horwitz function (blue regression line).

Conclusion: We should do better at low Pb concentrations.

Analytical comparability (1995-2007)

Element	Regression equation y = CV% x = Concentraiton mg/kg	n	scope mg/kg	Threshold value	mg/kg	-2 STD mg/kg	+ 2 STD mg/kg	2 CV %
Cd-tot	log y = 1.344-0.590 log x	198	0.01 - 14	RW	0.8	0.40	1.20	50.4
				PW	2	1.41	2.59	29.3
				SW	30	---	---	---
Co-tot	log y = 1.592-0.567 log x	209	0.14 - 52	RW	25	21.9	28.1	12.6
Cr-tot	log y = 1.798-0.363 log x	210	0.91 - 175	RW	50	34.9	65.1	30.3
Cu-tot	log y = 1.531-0.333 log x	211	0.27 - 155	RW	40	32.0	48.0	19.9
				PW	150	131	169	12.8
				SW	1000	---	---	---
Hg-tot	log y = 1.230-0.349 log x	207	0.004 - 4	RW	0.5	0.28	0.72	43.3
Mo-tot	log y = 1.288-0.597 log x	140	0.05 - 4	RW	5	---	---	---
Ni-tot	log y = 1.742-0.487 log x	210	0.75 - 284	RW	50	41.8	58.2	16.4
Pb-tot	log y = 1.768-0.357 log x	210	1.36 - 2463	RW	50	35.5	64.5	29.0
				PW	200	165	235	17.7
				SW	2000	1845	2155	7.8

(Ammann et al. 2008, extract)

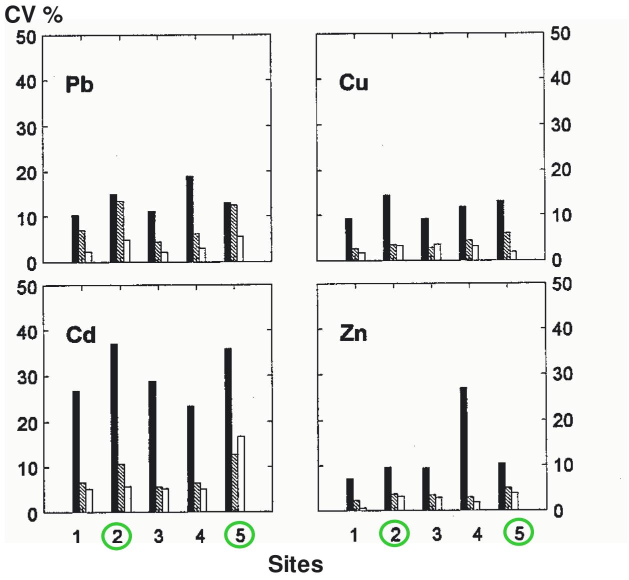


The variations decrease with increasing reproducibility conditions from a) to c). Note: The greatest effect is due to **analysis in different labs** and not to different sampling under similar soil conditons.

The variations of Cu and Zn are generally smaller and more stable than for Pb and Cd.

There is no clear difference of the variations between the different sites.

Measurement round robin (2)



a) Black column: Different sampling and analysis (n = 12-14)

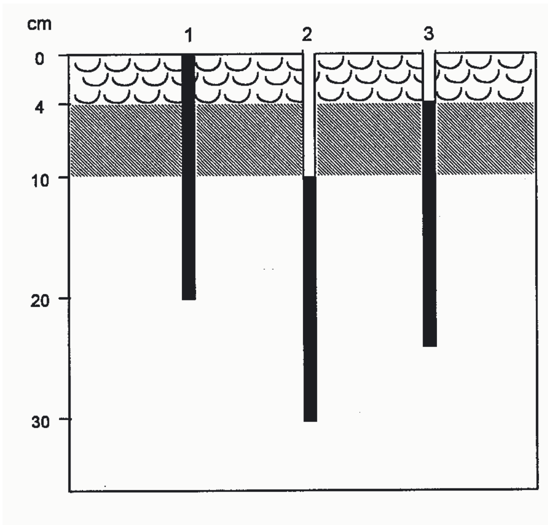
b) Grey column: Different sampling, same analysis (n = 13-14)

c) White column: Same sampling and analysis (n = 4)

(Desaules et al. 1994)

The forest sites 2 (coniferous forest) and 5 (deciduous forest) show no particularity.

Measurement round robin (3)
- Different sampling depth -



(Desaules et al. 1994)

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No distinct effect could be observed by the different sampling depth of the 20 cm cores (black), due to different layer bulk densities and probably selective elimination of litter at <2mm sieving.

References

A presentation of Pierre Gy's Sampling Theory and Practice is available in English under:

www.nabo.admin.ch >**Presentation**: NABO-Quality: Q001

• References see: www.nabo.admin.ch >**Bibliography**

• References of the sampling theory and practice:

Gy, P., 1998: Sampling for Analytical Purposes. John Wiley; Chichester. 153 p. ISBN 0 471 97956 2

Pitard, F.F., 1993: Pierre Gy´s Sampling Theory and Sampling Practice – Heterogeneity, Sampling Correctness, and Statistical Process Control. (2nd ed.), CRC Press, Washington D.C. 488 p. ISBN 0-8493-8917-8