

Nonparametric Uncertainty Analysis in Field Scale Application of Extended Sorption Isotherms – A Field Study –

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INTRODUCTION & OBJECTIVES

Background

Pedotransferfunctions (PTF) estimating the sorbed solid phase trace element concentration based on extended Freundlich isotherms have been derived for soils used as arable land (Utermann et al. 2005)

- PTF were derived by regression with point scale data on a national scale but trace element concentrations are needed on the field scale for legislative purposes
- ANOVA of the residual error (Altfelder et al. 2007) showed 70% of the variance originates from the field scale
 - What are the sources of the field scale variation? Uncertainty? Variability?

Aim

Uncertainty analysis in field scale application of extended sorption isotherms

Problem

Parametric assumptions often do not hold in soil science or problems arise from the need to (log) transform and retransform right skewed data

Approach

Nonparametric, i.e. distribution free estimators, to describe the samples can be a solution
Uncertainty of nonparametric estimators can be estimated by bootstrap percentile confidence intervals (Efron 1993)

MATERIAL & METHODS

Measure:

- Physicochemical soil properties V_i (pH, C_{org} , CEC, Mn_{ox})
- Trace element concentration in $Ca(NO_3)_2$ extract C
- Exchangable solid phase trace element concentration in Na_2 -EDTA extract S_{EDTA}

Predict:

- potentially exchangeable trace element concentrations S_{PTF} with extended Freundlich isotherms (PTF) using measured soil properties

$$S_{PTF} = K \times C^m = K_{in} \times \prod_{i=1}^k V_i^{\beta_i} \times C^m$$

S_{PTF} – adsorbat/adsorbent [$\mu\text{g}/\text{kg}$]
 K – Freundlich coefficient [$\mu\text{g}^{1-m} \text{P}/\text{kg}$]
 K_{in} – intrinsic Freundlich coefficient [$\mu\text{g}^{1-m} \text{P}/\text{kg}$]
 V_i – sorption parameter (pH, C_{org} , CEC, Mn_{ox})
 β_i – parameter coefficient
 C – adsorbat in $Ca(NO_3)_2$ solution [$\mu\text{g}/\text{l}$]
 m – Freundlich exponent [-]

- Coefficients of the PTFs with the highest coefficient of determination on the training data set by Utermann et al. (2005)

	$\log K_{in}$	β_{pH}	$\beta_{C_{org}}$	β_{CEC}	$\beta_{Mn_{ox}}$	m	R^2
Cd	-1.318	0.424	0.298	0.772		0.844	0.93
Cr	3.09					0.799	0.66
Cu	0.41	0.235		0.705		0.76	0.79
Ni	-0.839	0.265		0.904		0.76	0.90
Pb	0.776	0.331		0.466	0.285	0.619	0.86
Zn	-0.453	0.389		0.746		0.569	0.89

Sources of field scale variation

Natural Variability

- variance due to heterogeneity of the natural environment - **cannot** be reduced by increased analytical efforts

$$IQR \text{ (Inter quartile range)} = (Q_3 - Q_1)$$

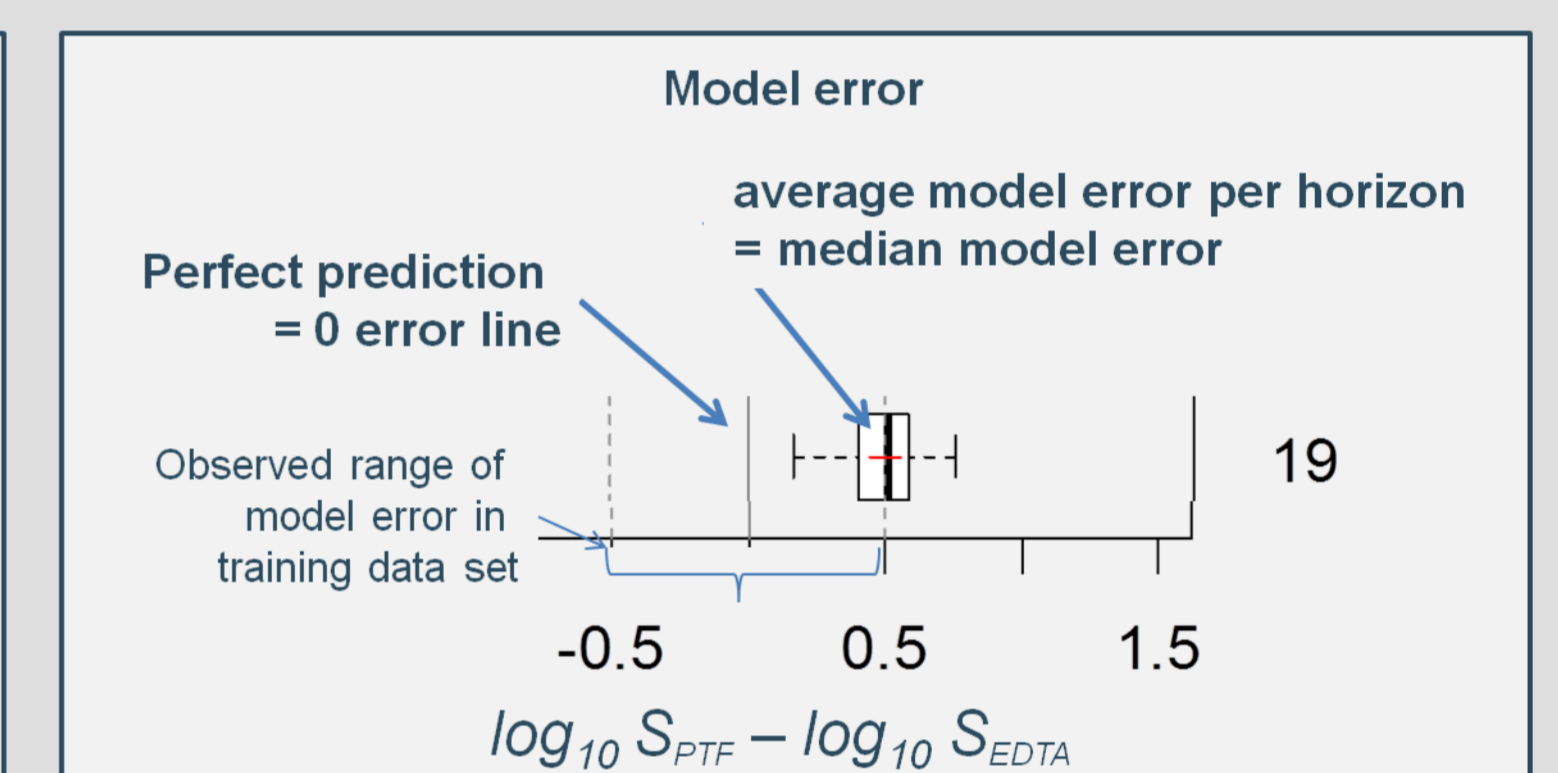
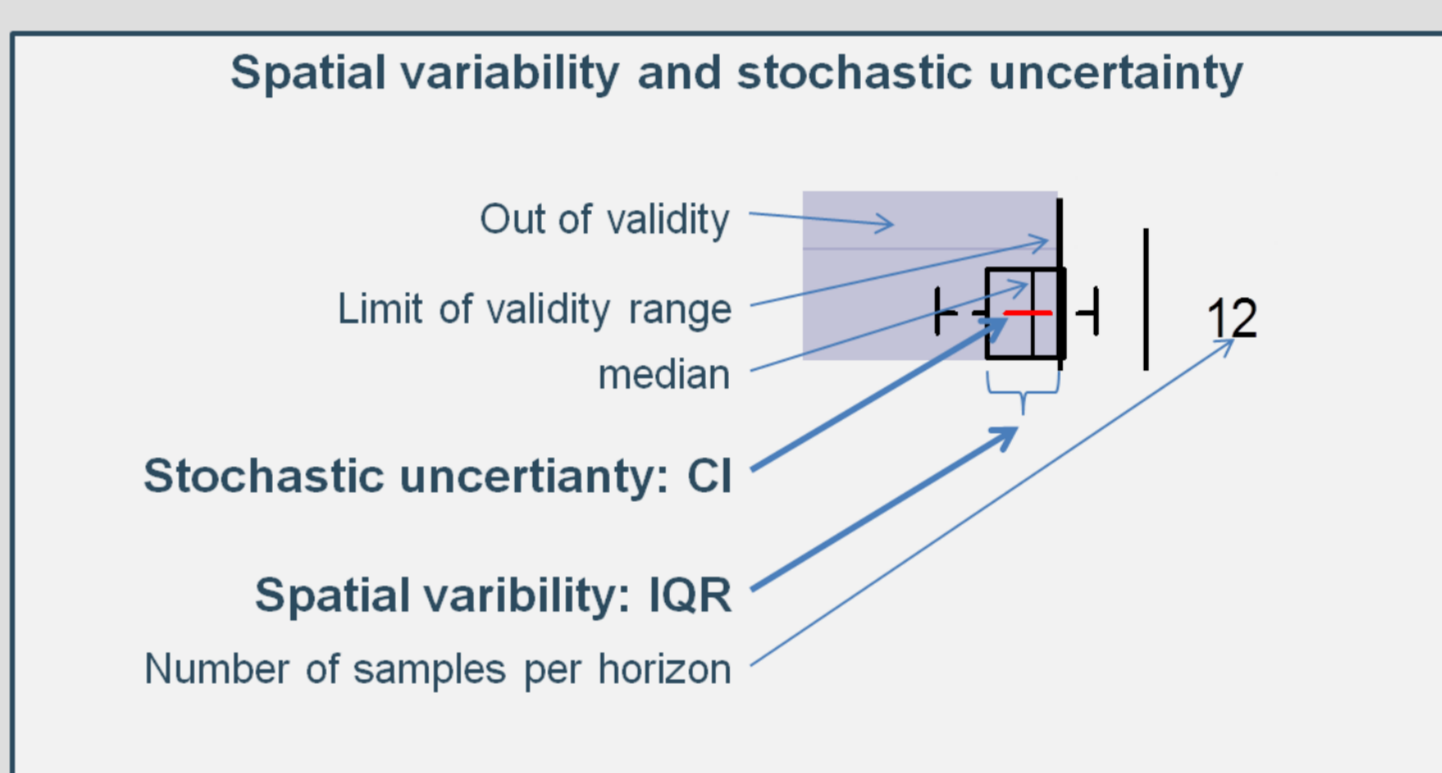
Informational or Knowledge Uncertainty

- Stochastic uncertainty** - variance due to lack of perfect information - **can** sometimes **be reduced** by e.g. increased samples or increased analytical efforts

CI = nonparametric bootstrap confidence interval $\alpha=0.1$; $R=8000$

- Model error** - bias due to the ignorance of systematic site specific factors governing the sorption of trace elements; **can be reduced** to some extent, for instance by local sorption isotherms

$$\log_{10} S_{PTF} - \log_{10} S_{EDTA}$$

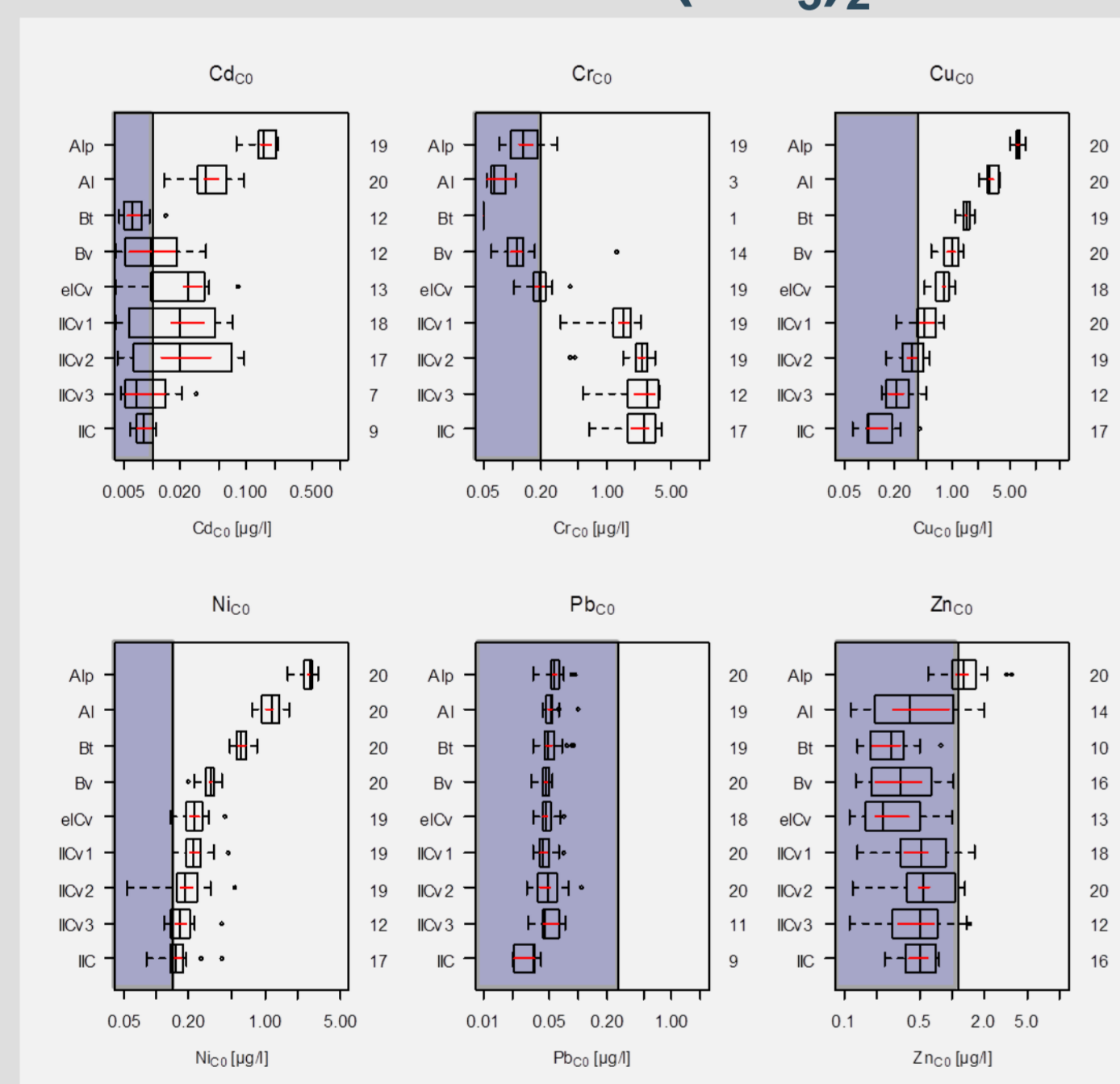


RESULTS

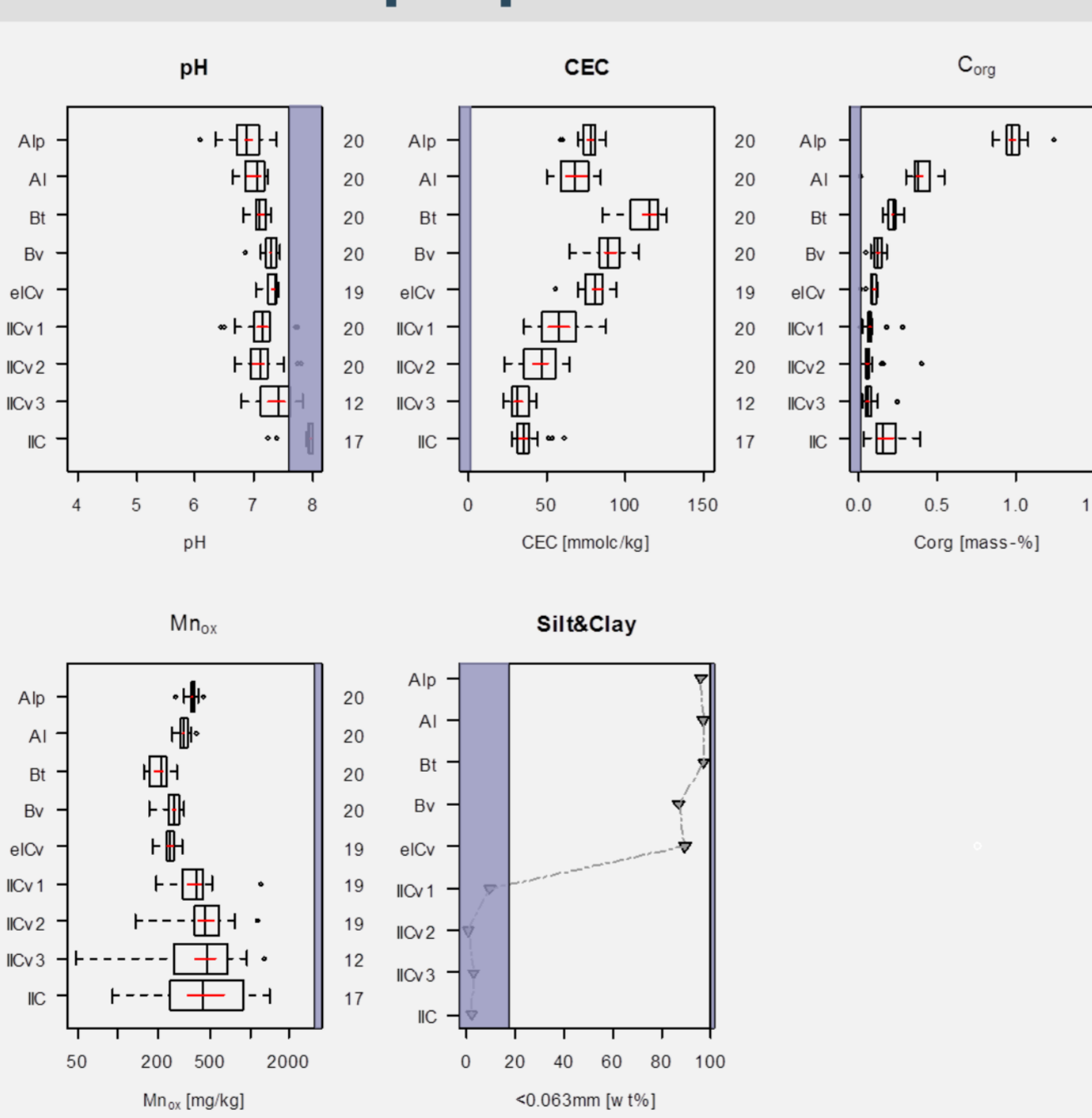
Characteristics of test soil haplic luvisol

(Input variables)

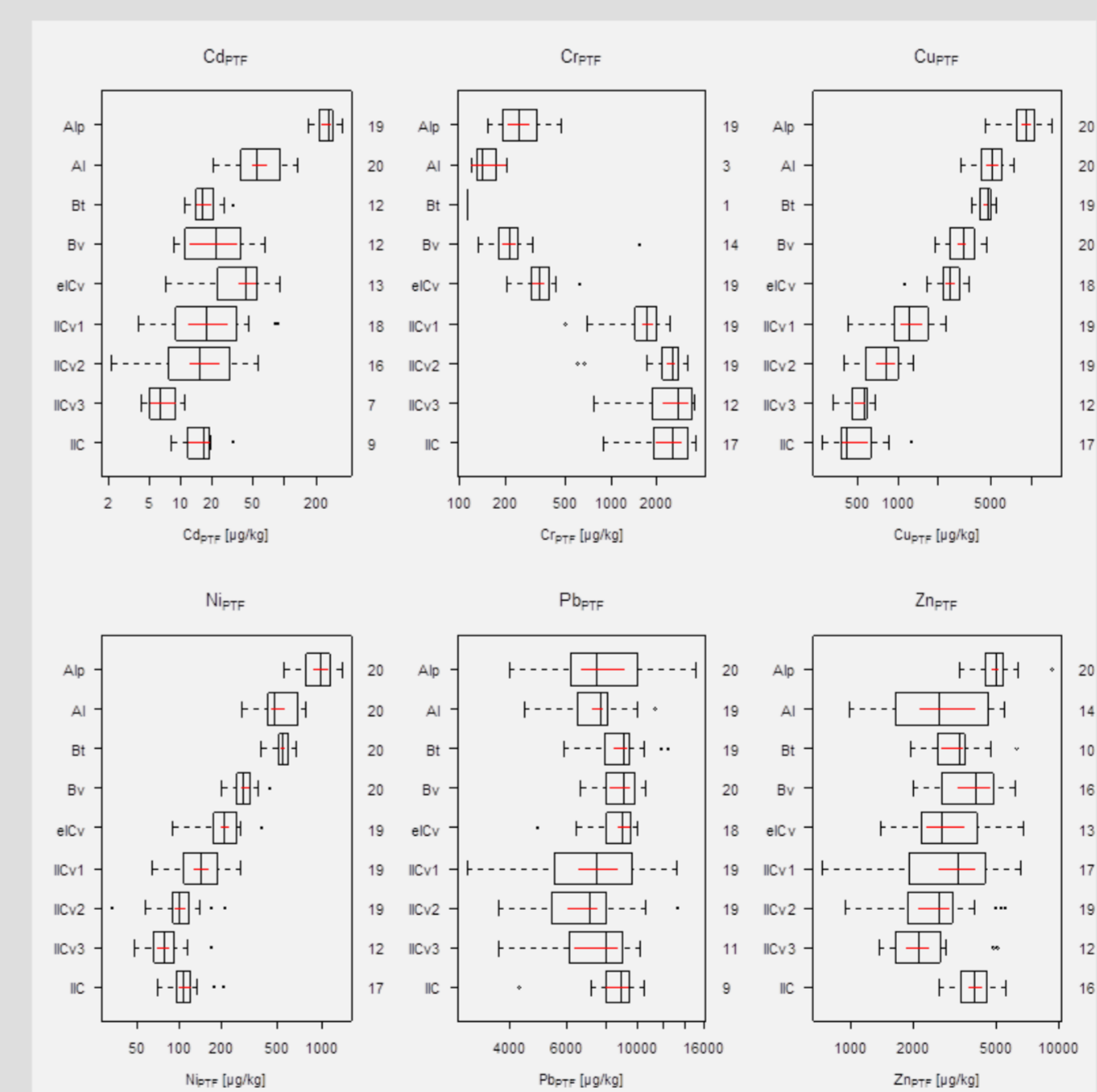
Measured trace element concentration in $Ca(NO_3)_2$ extract



Measured physicochemical soil properties

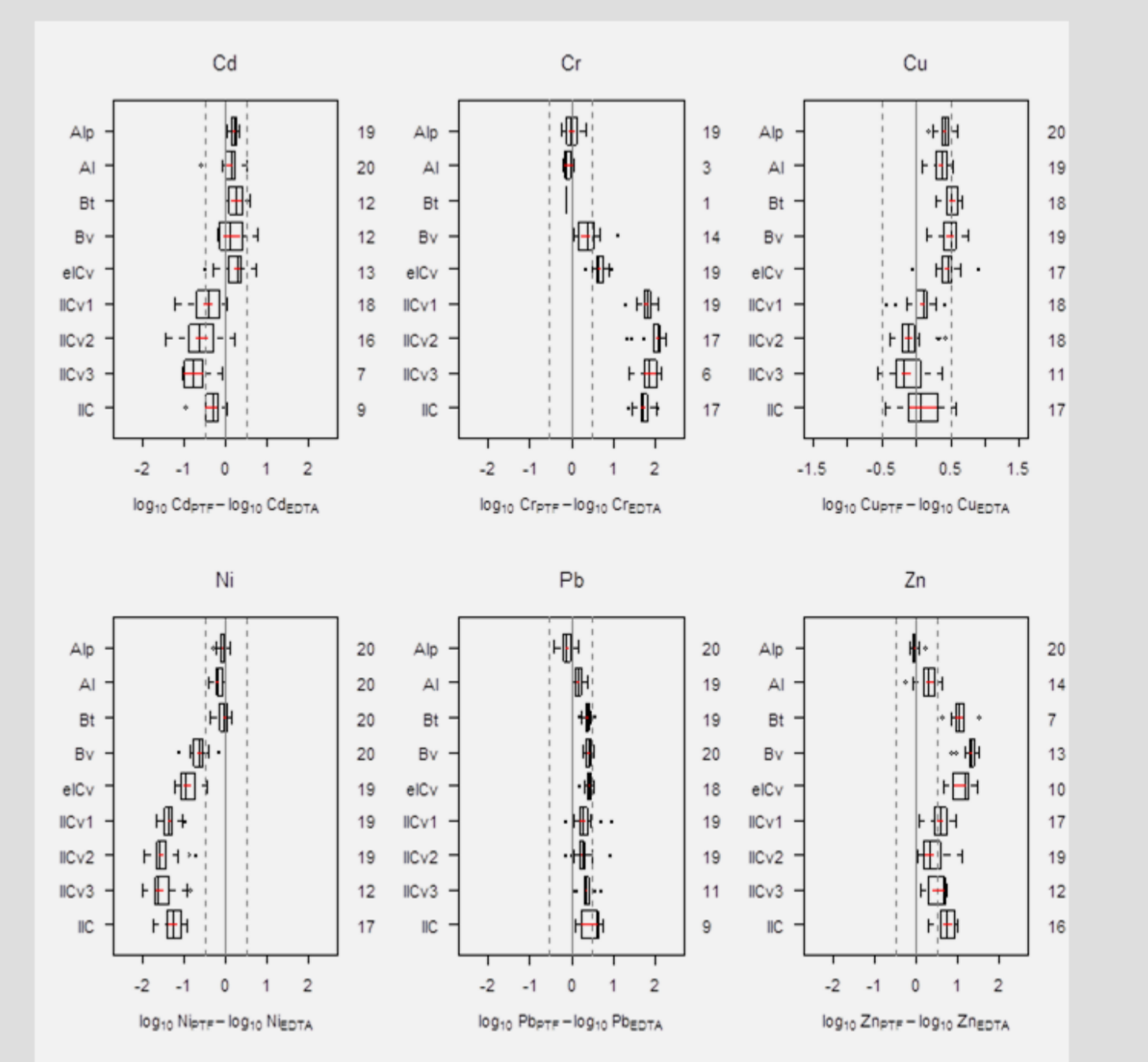


Spatial variability and stochastic uncertainty of predicted concentrations S_{PTF}



Model error of predicted concentrations

$$\log_{10} S_{PTF} - \log_{10} S_{EDTA}$$



- Total uncertainty relative to the concentration level is smallest in A horizons
- Spatial variability vertically often greater than horizontally (e.g. Cd, Cr, Cu and Ni)
- If physicochemical soil properties are well within the range of validity the main source of variation is the natural variability, e.g. Pb, Ni in A horizons

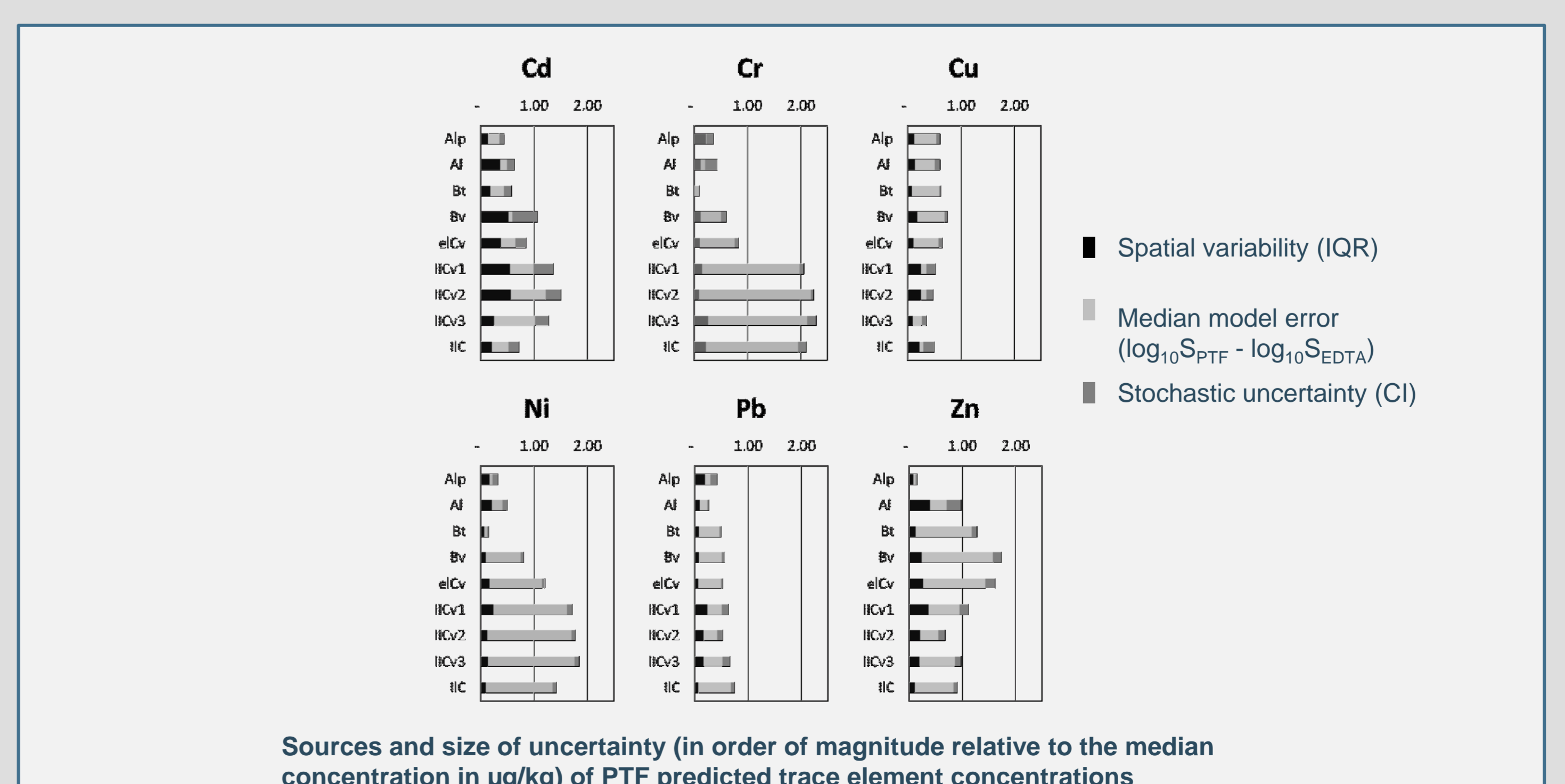
Model error main source of uncertainty in predictions made for Cr, Cu, Ni, Pb and Zn

Sources of model error. e.g.:

- Unspecific extracting agent
- $pH > 7$: precipitation in addition to sorption for some elements (e.g. Ni) → discontinuous increase of immobilization
- Soluble trace element concentrations deceeding the lower limit of validity is no significant cause of model error

Explanation: changes in singular physicochemical characteristics can lead to structural changes of demobilization mechanisms (e.g. $pH > 7$), deceedance of concentration levels does not have this effect

Total uncertainty of S_{PTF}



CONCLUSIONS

- When applied to soils with physicochemical parameters well within the range of validity extended sorption isotherms are a reliable tool
- Soluble trace element concentrations lower than the range of validity do not necessarily lead to model error

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