

**Sources of uncertainty in precautionary risk assessment of mobile
and potentially mobile trace elements in the soil groundwater
pathway**

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Kurzfassung

Ziel dieser Arbeit war die Analyse und Quantifizierung der räumlichen Variabilität im Zusammenhang mit der Unsicherheit in Methoden der vorsorgenden Risikobewertung für Spurenelemente im Pfad Boden-Grundwasser. Räumliche Variabilität ist ein Charakteristikum der Natur und kann im Gegensatz zu Quellen der wissensbasierten Unsicherheit, wie z.B. Modellfehler oder stochastische Unsicherheit, nicht durch höheren Untersuchungsaufwand verringert werden. Die mit der Risikobewertung für Spurenelemente im Pfad Boden-Grundwasser verbundene Unsicherheit wurde anhand von drei methodischen Beispielen der orientierenden Risikobewertung eruiert. Im ersten Beispiel wurde der Einfluss von räumlicher Variabilität im Feldmaßstab (10^2 m) und im Regionalmaßstab $\geq (10^5$ m) auf die Repräsentativität von Hintergrundwerten von Spurenelementkonzentrationen im Sickerwasser und auf die Anwendbarkeit von Geringfügigkeitsschwellenwerten anhand eines Kollektivs von $N = 418$ Sickerwasser-Proben von 46 Standorten untersucht. Die ausgewählten Standorte sind hinsichtlich Landnutzung, Grundwasserspiegel sowie ihrer Königswasser-extrahierbaren Spurenelementgehalte in der Festphase repräsentativ für die Norddeutsche Tiefebene. Konzentrationen von As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn und F wurden im Sickerwasser vom Übergang zwischen der ungesättigten zur gesättigten Zone, dem Ort der rechtlichen Beurteilung, analysiert. Mediane und 90. Perzentile der Hintergrundkonzentrationen im Sickerwasser wurden mit ihren entsprechenden Geringfügigkeitsschwellen verglichen. In mehr als 10% aller Proben überschritten die Hintergrundkonzentrationen von Cd, Co, Ni, V oder Zn die Geringfügigkeitsschwellenwerte. Die räumliche Variabilität der Konzentration von Cd, Zn, Mo, Pb, Co und Ni konnte zu einem Großteil durch die räumliche Variabilität der pH-Werte erklärt werden. Die Sickerwasserkonzentrationen von Sb, As, Cr, Cu, und V korrelierten signifikant mit der Konzentration an gelöstem organischem Kohlenstoff. Demzufolge konnte die Repräsentativität der Hintergrundwerte durch Stratifikation der Hintergrundkonzentrationen in Gruppen ähnlicher pH-Werte bzw. ähnlicher DOC-Konzentration verbessert werden. Bodenausgangsgestein und Landnutzungsform haben erheblichen Einfluss auf die physikochemischen Eigenschaften der Böden, sodass Böden von Gruppen vergleichbarer Bodenausgangsgesteine und Landnutzungsformen ähnliche physikochemische Eigenschaften aufweisen. Daher kann auch eine Stratifikation nach

Gruppen vergleichbarer Bodenausgangsgesteine und Landnutzungsformen eine Verbesserung der Repräsentativität von Hintergrundwerten von Spurenelementen im Sickerwasser erzielen. Der große Einfluss der feldskaligen Variabilität auf die Unsicherheit von Medianen zeigte sich darin, dass Aussagen über die Über- oder Unterschreitung von Geringfügigkeitsschwellenwerten innerhalb eines Standorts nur mit annehmbarer statistischer Unsicherheit ($\alpha \leq 0,1$ Bootstrap-Konfidenzintervall des Medians) möglich war, wenn die fraglichen Mediankonzentration etwa 1/3 höher oder niedriger als der entsprechende Geringfügigkeitsschwellenwert war.

In situ Beprobungen von Sickerwasser sind oft zu zeitaufwendig oder kostspielig für Fragestellungen der orientierenden Risikobewertung. Daher werden Spurenelementkonzentrationen in Batch-Extrakten oft als Ersatz für in situ Konzentrationen verwendet. Um die mit der Batch-Extraktion verbundene Unsicherheit zu untersuchen, wurden Konzentrationen von Spurenelementen in Batch-Extrakten zweier gängiger Methoden ihren Äquivalenten im Sickerwasser gegenübergestellt, wobei Sickerwasser und Bodenmaterial der 250 Probenpaare von jeweils exakt dem gleichen Ort am Übergang zwischen ungesättigter und gesättigter Zone im Boden stammte. Die Wasser-Feststoff-Verhältnisse der Extraktionsversuche betrug 2 l/kg und 5 l/kg, wobei die Ionenstärke des 5 l/kg Extrakts mit $\text{Ca}(\text{NO}_3)_2$ an in situ Konditionen angepasst wurde. Die Konzentrationen der meisten Spurenelemente zeigten im Extrakt eine statistisch signifikante (p -Wert < 0.01), aber schwache Korrelation mit ihren entsprechenden in situ Konzentrationen. Im 2 l/kg Extrakt zeigten Pb und Cr eine ungenügende Vergleichbarkeit mit ihren in situ-Äquivalenten. Für die anderen Elemente erhöhte sich die Korrelation in der Reihenfolge $\text{As} < \text{Cu}, \text{Zn}, \text{Sb}, \text{Mo}, \text{V} < \text{Cd}, \text{Ni}, \text{Co}$, wobei die Anpassung der Ionenstärke i.d.R. zu etwas besseren Ergebnissen hinsichtlich ihrer Richtigkeit bei kationischen Elementen führte. Zusätzlich zu den elementspezifischen Mängeln, schien es, dass niedrige in situ Konzentrationen in der Regel durch Batch-Extraktions-Methoden unterschätzt wurden. Systematische Abweichungen der Konzentrationen im Batch-Extrakt von in situ Konzentrationen konnten für einige Elemente durch Einstellen der Ionenstärke reduziert werden. Allerdings änderte die Anpassung der Ionenstärke wenig an der Unsicherheit durch nicht erklärbare Varianz, welche für beide Extraktionsmethoden ähnliche Größenordnungen zeigte. Ausgedrückt in Prognoseintervallen ($\alpha = 0,1$) der Regressionsgeraden, betrug die Unsicherheit durch nicht erklärbare Varianz 0,44 - 0,77 Größenordnungen, während die Unsicherheit durch

kleinräumige Variabilität 0,22 - 0,42 Größenordnungen betrug. Die nicht erklärbare Varianz führte dazu, dass Spurenelementkonzentrationen im 2 l/kg Extrakt nur dann mit ausreichender statistischer Sicherheit ($\alpha \leq 0,1$) verwendet werden konnten, um eine in situ Überschreitung von Geringfügigkeitsschwellenwerten vorherzusagen, wenn ein Sicherheitsabstand von ca. einer Größenordnung höher als der zur Debatte stehende Geringfügigkeitsschwellenwert berücksichtigt wurde. Angesichts der geringen Verbesserung der Genauigkeit ist es fraglich, ob die leichte Verringerung systematischer Abweichungen den recht hohen methodischen Aufwand der 5 l/kg Extraktion mit angepasster Ionenstärke rechtfertigt.

Anhand einer Unsicherheits- und Sensitivitätsanalyse für die Anwendung von substratübergreifenden Sorptionsisothermen sog. Pedotransfer-Funktionen (PTF) am Beispiel zweier für die Norddeutsche Tiefebene typischen Böden, wurde die Unsicherheit infolge kleinräumiger Variabilität im Feldmaßstab in Relation zu stochastischer Unsicherheit und zum Modellfehler untersucht. Um die Grenzen der Anwendbarkeit der PTF aufzuzeigen, wurden Böden gewählt, deren Eigenschaften am Rande der Gültigkeitsbereiche der angewandten Sorptionsisothermen lagen. Für Böden mit $\text{pH} > 6,5$, obwohl im Prinzip innerhalb des Gültigkeitsbereichs, war der Modellfehler die Hauptursache der Unsicherheit, da Sorption hier nicht der vorherrschende Retentionsmechanismus war. In Böden, in denen Sorption der vorherrschende Retentionsmechanismus ist, war der Modellfehler mit durchschnittlich 0,2 - 0,3 Größenordnungen vergleichsweise gering. Die räumliche Variabilität im Feldmaßstab, quantifiziert durch den Inter-Quartil-Abstand (geschätzt von $N = 10 - 20$ Proben je Horizont), war mit 0,1 - 0,6 Größenordnungen in diesen Fällen die dominierende Quelle der Unsicherheit für die Vorhersagemediankonzentrationen der potentiell austauschbaren Spurenelementfraktion.

Für $N > 10$ Proben war das Konfidenzintervall ($\alpha = 0,1$) des Medians von Spurenelementkonzentrationen kleiner als der Inter-Quartil-Abstand. Dies bedeutet, dass der Medianwert für diese Anzahl von Proben eine höhere Aussagekraft für die zentrale Tendenz hat als eine einzelne Probe. Für $N \leq 10$ Proben allerdings war das durchschnittliche Konfidenzintervall des Medians ($N = 46$ Standorten) ähnlich weit oder weiter als der durchschnittliche Inter-Quartil-Abstand der Spurenelementkonzentrationen im Sickerwasser innerhalb eines Standortes. Das bedeutet, dass bei der vorgefundenen räumlichen Variabilität im Feldmaßstab Stichprobengrößen von $N \leq 10$ nicht ausreichend sind, um dem

Median eine stärkere Aussagefähigkeit über die zentrale Tendenz zu verleihen als eine einzelne Probe haben würde.

Schlagworte: Wirkungspfad Boden-Grundwasser, Spurenelemente, Unsicherheit

Abstract

The objective of this study was to analyze and quantify the role of spatial variability in uncertainty in the context of precautionary risk assessment of trace elements in the soil groundwater pathway. Spatial variability is a property of nature and cannot, in contrast to informational sources of uncertainty, be reduced. Uncertainty was studied with reference to three examples with an increasing volume of sources of uncertainty. In the first example, uncertainty in risk assessment was studied for the current risk in groundwater contamination based on percolation water samples. An examination was made of the influence of field scale ($\leq 10^2$ m) and national scale ($\geq 10^5$ m) spatial variability of trace element concentrations in percolation water on the representativeness of background values and applicability of insignificance thresholds. This examination was based on a sample collection of $N = 418$ percolation water samples from 46 sites. These sites were representative for the Northern German lowlands in terms of land use, parent material depth of groundwater table and total (aqua-regia extractable) solid phase background concentrations of trace elements. Concentrations of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn and F were analyzed in percolation water from the transition from unsaturated to saturated zone. Median and 90th percentile values of background concentrations were compared with German insignificance thresholds. In more than 10% of all samples, background concentrations of Cd, Co, Ni, V or Zn exceeded the insignificance thresholds. The representativeness of background values could be increased by either stratifying background concentrations according to groups of similar pH or according to groups of similar DOC concentration. Since parent material and land use affect the physicochemical properties of the soil, which in turn affect the trace element concentration in percolation water, stratification according to parent material and land use also made it possible to increase the representativeness of the background values of trace elements in percolation water. The influence of field scale variability on the precision of field scale medians of background concentrations was evaluated, taking into consideration field-scale interquartile distance and the bootstrap percentile confidence interval of the field scale median. Statements concerning the exceedance or nonexceedance of threshold values could only be made with acceptable statistical uncertainty ($\alpha \leq 0.1$) when operational median concentrations were approx. 1/3 higher or lower than the corresponding insignificance threshold.

Sampling of in situ percolation water is often too time-consuming or expensive for the purpose of exploratory investigations in precautionary risk assessment. Trace element concentrations in batch extracts are often used as a surrogate for in situ concentrations. A comparison was made of two popular procedures to investigate dissolved trace element concentration in soil water using 250 sample pairs of percolation water and soil samples which were taken concurrently in the transition zone of the soil. These samples of in situ percolation water were used to measure in situ concentrations, while solid soil material was used to measure trace element concentrations at two liquid/solid ratios using batch experiments. The liquid-solid ratios were 2 l/kg and 5 l/kg. At 5 l/kg the ionic strength was adjusted with $\text{Ca}(\text{NO}_3)_2$ to a sample specific value similar to in situ, while at 2 l/kg the ionic strength was not adjusted. The concentrations of most trace elements extracted exhibited a statistically significant but weak correlation ($p\text{-value} < 0.01$) to their corresponding in situ concentrations. In the liquid-solid ratio of 2 l/kg extracts, Pb and Cr showed very poor comparability with the in situ equivalent. For the other elements, correlation increased in the order $\text{As} < \text{Cu}, \text{Zn}, \text{Sb}, \text{Mo}, \text{V} < \text{Cd}, \text{Ni}, \text{Co}$. Adjustment of the ionic strength led to a slightly more marked correlation. In addition to element-specific shortcomings, it appeared that low concentration levels of in situ concentrations were generally underestimated by batch extraction methods. The liquid-solid ratio of 2 l/kg extracts could only be used as a method to predict exceedance of thresholds when a safety margin of approximately one order of magnitude higher than the thresholds was adopted. When using trace element concentrations in batch extracts to estimate the central tendency of concentrations in situ, significant inaccuracy and imprecision have to be expected over and above the uncertainty resulting from spatial variability. Inaccuracy could to some extent be reduced by adjusting one parameter to in situ conditions. The estimates of in situ concentrations by both batch extraction methods were equally imprecise. Expressed in prediction intervals ($\alpha = 0.1$) characterizing the uncertainty of the single estimate, uncertainty due to imprecision in batch extraction was as large as orders of magnitude of between 0.44 and 0.77, while field scale variability ranged between 0.22 and 0.42 within 90 m. The imprecision of batch extracts was the largest source of uncertainty within all the studies undertaken for this thesis and could not be significantly reduced by adjusting the ionic strength to in situ conditions. Given the small improvement in precision it is questionable whether the slight improvement in accuracy justifies the laborious protocol of the 5 l/kg extraction with adjusted ionic strength.

In a non-parametric uncertainty and sensitivity analysis for the application of semi-empirical general-purpose sorption isotherms, so-called pedotransfer function (PTF) uncertainty resulting from field scale variability was studied in relation to model error and stochastic uncertainty. This uncertainty analysis was conducted on two soils, which were both characteristic for the Northern German Lowlands and were in one or more of their properties at the edge of the range of validity of the sorption isotherms applied. In soils with $\text{pH} > 6.5$, although technically within the range of validity, model error was the main source of uncertainty, because sorption was no longer the predominant retention mechanism. In soils in which sorption was the predominant retention mechanism, the model error was fairly low (median model error was in the order of magnitude of 0.2 - 0.3). For these cases spatial variability quantified by the inter-quartile distance of $N = 10-20$ samples was the predominant source of uncertainty (order of magnitude of 0.1 - 0.6).

For $N > 10$ samples the confidence interval ($\alpha = 0.1$) of median trace element concentrations was always smaller than the inter-quartile distance, showing that the median for sample sizes $N > 10$ was a more powerful estimate of the central tendency than an individual sample. For $N \leq 10$ samples, the average size of the confidence interval estimated for 46 field scale median trace element concentrations in percolation water was as wide as, or in one case wider than, the average field scale inter-quartile distance, suggesting that sample sizes of $N \leq 10$ are not great enough to estimate a median that is a more powerful estimate of the central tendency than an individual sample.

Keywords: Soil-groundwater pathway, trace elements, uncertainty

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Abbreviations

°C	degree Celsius
Al	aluminium
Al	clay deprived topsoil horizon
Alp	clay deprived topsoil horizon with clear signs of tillage
α	Cronbachs alpha, coefficient of reliability
As	arsenic
Ap	topsoil horizon with clear signs of tillage
As _{EDTA}	Na ₂ -EDTA extractable arsenic [$\mu\text{g}/\text{kg}$]
a _T	axis intercept calculated with log ₁₀ -transformed data
b	constant term for the slope in linear model
Ba	barium
BaCl ₂	barium chloride
Ba _{EDTA}	Na ₂ -EDTA extractable barium [$\mu\text{g}/\text{kg}$]
BAG 1000	Parent Material Groups Map of the Federal Republic of Germany 1:1,000,000
BBodSchV	German Federal Soil Protection and Contaminated Sites Ordinance
BCa	bias-corrected and accelerated nonparametric bootstrap confidence interval
β_i	standardized regression coefficient of an input variable
Bt	clay rich horizon
BÜK 1000	Soil Map of the Federal Republic of Germany 1:1,000,000
Bv	weathered subsoil horizon
C	soluble concentration of the trace element [$\mu\text{g}/\text{l}$]
c	constant term for the slope in linear model regression coefficient
C0	native trace element concentration in percolation water [$\mu\text{g}/\text{l}$]
Ca	calcium
Ca(NO ₃) ₂	calcium nitrate
CaCl ₂	calcium chloride
Cd	cadmium
Cd _{EDTA}	Na ₂ -EDTA extractable cadmium [$\mu\text{g}/\text{kg}$]
Cd _{PTF}	PTF estimate of cadmium [$\mu\text{g}/\text{kg}$]

CEC	cation exchange capacity [mmol _c /kg]
CI	confidence interval
CI _{np}	nonparametric confidence interval
CI _p	parametric confidence interval
Co	cobalt
Co _{EDTA}	Na ₂ -EDTA extractable cobalt [μg/kg]
C _{org}	organic carbon [mass-%]
COV	coefficient of variation
Cr	chromium
CrO ₄ ²⁻	chromate ion
CrOH ²⁺	chromium hydroxide ion
Cr _{PTF}	PTF estimate of chromium [μg/kg]
Cu	copper
Cu _{EDTA}	Na ₂ -EDTA extractable copper [μg/kg]
Cu _{PTF}	PTF estimate of copper [μg/kg]
Cv	weathered underground horizon
DOC	dissolved organic carbon [mg/l]
DOC _{extract}	dissolved organic carbon in batch extract [mg/l]
DOC _{insitu}	dissolved organic carbon in in situ sampled percolation water [mg/l]
EC	electric conductivity [μS/cm]
EC ₂₁	electric conductivity in 2 l/kg extract [μS/cm]
EC ₅₁	electric conductivity in 5 l/kg extract with adjusted ionic strength [μS/cm]
EC _{extract}	electric conductivity in batch extract [μS/cm]
EC _{insitu}	electric conductivity in in situ sampled percolation water [μS/cm]
eICv	unconsolidated lime rich weathered underground horizon
F	flour
Fe	iron
Fe _{ox}	oxalate soluble iron [mg/kg]
FEP	fluorinated ethylene propylene
g	g-force
GFS	German insignificance threshold for trace elements in groundwater

Go(Cv)	gleyic horizon under mainly oxidative conditions also showing properties of a weathered underground horizon
H ⁺	free hydrogen ion activity [mol/l]
H ⁺ _{extract}	free hydrogen ion activity in batch extract [mol/l]
H ⁺ _{insitu}	free hydrogen ion activity in in situ sampled percolation water [mol/l]
H ₂ O	water
HCl	hydrogen chloride
HNO ₃	nitric acid
HÜK 200	Hydrogeological Map of the Federal Republic of Germany 1: 200,000
IC	ion chromatography
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
int	y-axis interception
IQD	inter quartile distance
K _d	partition coefficient [kg/l]
K _f	Freundlich coefficient [$l^m \mu g^{1-m} / kg$]
K _{f-in}	intrinsic Freundlich coefficient [$l^m \mu g^{1-m} / kg$]
LABO	Federal / State Working Group on Soil Protection
LAWA	German Working Group on water issues of the Federal States and the Federal Government represented by the Federal Environment Ministry
LBEG	State Authority for Mining, Energy and Geology
LL/A	loess or glacial loam/ arable land
log ₁₀	decadic logarithm
LOQ	limit of quantification
LS	liquid solid ratio
m	Freundlich exponent [-]
MAE	median absolute model error
Me ^{y+}	free metal ion
Me ^{z+}	free metal ion
Me(NO ₃) ₂	metal-nitrate-complex
MeCl ₂	metal-chloride-complex

MeOH	metal-oxide-complex
min	minute
Mn	manganese
Mn _{ox}	oxalate soluble manganese [mg/kg]
Mo	molybdenum
Mo _{EDTA}	Na ₂ -EDTA extractable molybdenum [μg/kg]
MoO ₄ ²⁻	molybdate ion
N	number of observations
Na ₂ -EDTA	disodium ethylenediaminetetraacetic acid
N _b	number of bootstrap replicates
Ni	nickel
Ni _{EDTA}	Na ₂ -EDTA extractable nickel [μg/kg]
Ni _{PTF}	PTF estimate of nickel [μg/kg]
NO ₃	nitrate
p	probability
P10 _{boot}	10th percentile of the population of bootstrap replicates of median
P ₂₅	25th percentile
P ₇₅	75th percentile
P90 _{boot}	10th percentile of the population of bootstrap replicates of median
Pb	lead
Pb _{PTF}	PTF estimate of lead [μg/kg]
pH	negative decadic logarithm of H ⁺ activity in solutions
pH ₂₁	pH-value in 2 l/kg extract
pH ₅₁	pH-value in 5 l/kg extract with adjusted ionic strength
pH _{insitu}	pH-value measured in in situ sampled percolation water
PTF	pedotransfer function based on general purpose Freundlich isotherms
PTFE	polytetrafluoroethylene
Q ₁	first quartile
Q ₃	third quartile
r ²	coefficient of determination
r ² adj	coefficient of determination adjusted to the sample size

ρ	coefficient of correlation
rpm	rounds per minute
S	potentially exchangeable concentration of trace element in solid soil phase [$\mu\text{g}/\text{kg}$]
S ₀	native potentially exchangeable trace element concentration of the soil solid phase [$\mu\text{g}/\text{kg}$]
SA/A	sand/ arable land
SA/F	sand/ forest
SA/G	sand/ grassland
Sb	antimony
Sb _{EDTA}	Na ₂ -EDTA extractable antimony [$\mu\text{g}/\text{kg}$]
S _{EDTA}	Na ₂ -EDTA extractable trace element concentration [$\mu\text{g}/\text{kg}$]
SbO ₃ ⁻	antimony(III)oxide ion
Sn	tin
Sn _{EDTA}	Na ₂ -EDTA extractable tin [$\mu\text{g}/\text{kg}$]
SOM	Soil organic matter
S _{PTF}	PTF estimate [$\mu\text{g}/\text{kg}$]
V	vanadium
V _{EDTA}	Na ₂ -EDTA extractable vanadium [$\mu\text{g}/\text{kg}$]
V _i	input variable of sorption relevant soil property
x _L	threshold limit of unknown independent variable
x _{Ti}	unknown independent variable calculated with log ₁₀ -transformed data
y _L	threshold limit of unknown dependent variable
y _{Ti}	unknown dependent variable calculated with log ₁₀ -transformed data
Zn	zinc
Zn _{EDTA}	Na ₂ -EDTA extractable zinc [$\mu\text{g}/\text{kg}$]
Zn _{PTF}	PTF estimate of zinc [$\mu\text{g}/\text{kg}$]

1 General Introduction

In Germany over 70% of consumed groundwater is obtained from juvenile groundwater resources which feed off percolation water (Federal Statistical Office 2007). Groundwater protection starts by protecting the soil. When soils are contaminated there is always a chance that the groundwater is or will be affected by this contamination as well. Exploratory investigations concerning trace elements are an instrument for precautionary soil protection and can be conducted by analyzing soil material, percolation water or groundwater (LABO 2003). While groundwater analysis can only confirm contamination, information gathered by percolation water or soil analysis enables estimates to be made of current and future contamination risks for the groundwater and additionally allows plans to be drawn up for precautionary measures to protect the groundwater.

To assess the risk for groundwater contamination in the vadose zone, when trace elements are the substance in question, soil or percolation water can be analysed. To assess the immediate risk for groundwater contamination, percolation water or soil samples from directly above the groundwater at the transition between the unsaturated and the water saturated zone in the soil can be sampled and analyzed (Figure 1). If future risks for groundwater contamination are in question, percolation water prognosis can be done. In percolation water prognosis the source strength is estimated based on analysis from the leaching behaviour of soil samples collected near the soil surface or from the leaching behaviour of substitute soil material e.g. used for landfills or construction. Based on the source strength and the physicochemical and hydrological properties of the unsaturated zone in between the place of sampling and the groundwater, percolation water prognosis will then be used to predict the timeframe and quantity in which the substance will reach the groundwater (LABO 2003). The transport behaviour of trace elements in percolation water is known to be more sensitive toward physicochemical properties of the soil than toward hydrological properties (Finke et al. 1996).

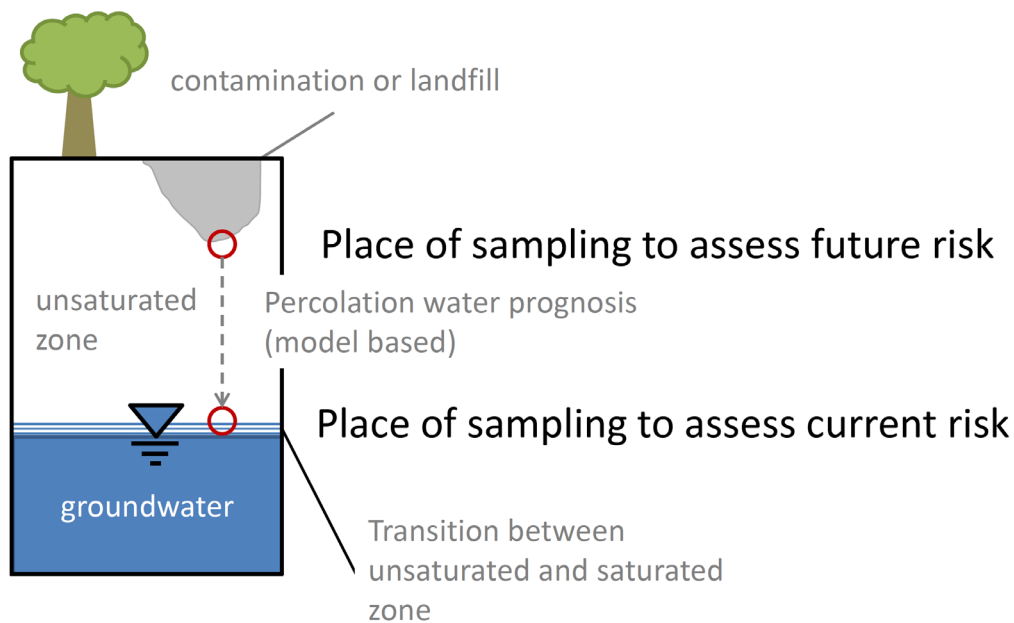


Figure 1: Schematic display of places of sampling in the soil for the purpose of exploratory risk assessment for groundwater contamination with trace elements

By comparing measured, estimated or predicted trace element concentrations with standards for good-quality soil or percolation water the degree of risk for groundwater contamination can be assessed. Local or regional background values of trace elements in the soil or percolation water can serve as adequate standards. Where background values are unknown, insignificance threshold concentrations can serve as standards instead. German insignificance thresholds for the groundwater (GFS), listed by the German Working Group on water issues of the Federal States and the Federal Government (LAWA 2004), are examples of such standards.

The underlying question of risk assessment for trace elements in the pathway soil groundwater is: how likely is it that a critical concentration, such as the GFS, is or will be exceeded in a particular area? The answer to this question, and thus the effectiveness of judiciary decisions, depends on the quantity and quality of the data collected as well as on the true properties of the soil, i.e. the variability of physicochemical soil properties and trace element concentrations (Bolker 2008). The quantity of the data mainly affects the uncertainty of measures of the central tendency within an area. The quality of the data affects both accuracy and precision. The accuracy of the answer indicates the correctness of the estimate, i.e. for example if an estimate or a prediction of trace element concentrations correctly reflects the situation in situ. The precision characterizes how detailed a value can be estimated (ibid.). Trace elements in percolation water in situ can be very variable within field scale dis-

tances ($\approx 10^2$ m), so that when a single measurement meets the threshold concentration in one place the concentration may easily be exceeded at another place at the same site. Accuracy is obviously more important than precision since a precise but wrong answer is useless (Bolker 2008).

1.1 Trace elements in the pathway soil groundwater

Trace elements can already be harmful to the environment in small concentrations. Trace elements are a group of elements which are naturally present in concentrations of $<0.1\%$ in the lithosphere (Adriano 2001). The elements considered in this study are As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn and F. Some of these elements e.g. Cu, Mo or Zn are essential for a well-functioning metabolism of plants and animals as constituents of enzymes (Allaby 2000). However, all trace elements bear a potential toxicity for plants and animals at elevated concentration levels (Adriano 2001).

Trace elements in the percolation water can originate from the parent material, flooding events, the atmosphere or direct input. Natural atmospheric sources of trace elements include for example volcanic ashes or eolian dusts. Additionally, in densely populated and highly industrialized countries such as Germany, anthropogenic sources for trace elements in percolation water cannot be ruled out even in rural areas. Anthropogenic sources for atmospheric depositions include aerosol emissions from industrial plants, cars, the metallurgical industry or as a consequence of generating energy from fossil resources (Adriano 2001). Ubiquitous direct input of trace elements can result from the use of soil amendments, such as fertilizers, limes and animal manure, as well as pesticides, herbicides or insecticides.

Soils are considered as a sink for trace elements. In contrast to organic contaminants trace elements are non-degradable and are thus persistent. Within the soil, trace elements occur in different stages of fixation ranging from the inert fraction within the crystal lattice of minerals through trace elements adsorbed into soil particles to dissolved trace elements in the percolation water (Figure 2). The ecologically most relevant form in the soil is the dissolved form in percolation water (Blume et al. 2010), which is easily accessible for plants and animals.

In temperate climates with acid to neutral soil pH the processes governing the mobilization of the ecologically relevant fractions of trace element concentrations are sorption and desorption. Sorption means the attachment of dissolved matter to the surface of soil particles

(Lewandowski et al. 1997). Complexation due to coordinative binding affected by electrostatic forces or shared electron pair binding is one possible binding mechanism of sorption (ibid.). Other sorts of binding are covalent binding, ion-binding or dipole-dipole interaction.

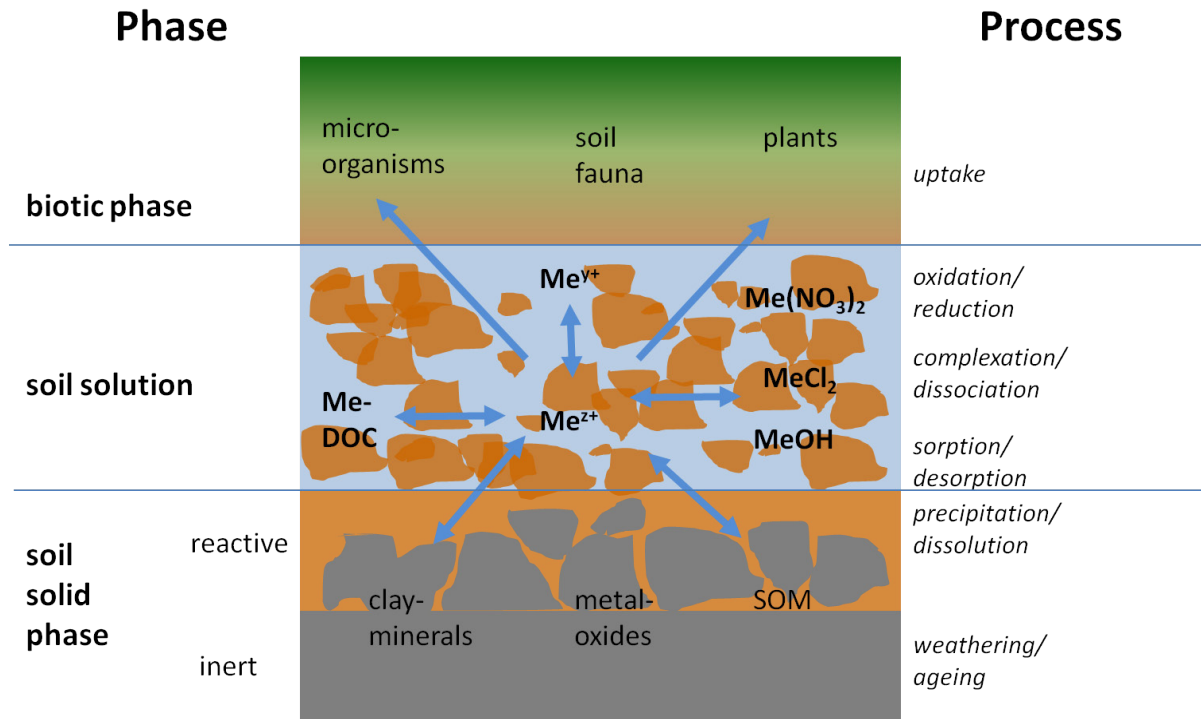


Figure 2: Chemical and biological availability of trace elements in the soil (following Groenenberg 2011). Me^{x+} and Me^{y+} = free metal ions of different redox stadiums, Me-DOC= dissolved metal-organic complex, $MeCl_2$, $Me(NO_3)_2$, $MeOH$ = inorganic metal complexes, SOM= soil organic matter

The soil's capacity to bind trace elements is limited. The mobility of trace elements depends on the physicochemical properties of the percolation water and the soil, such as the pH, cation exchange capacity, redox potential and content and quality of hydroxides, clay and organic carbon in the soil. The pH value is an important influence on the mobility of trace elements, because it affects the mobility of trace element and of potential complexation ligands, such as humic acids or metal oxides in the soil solution. Generally a rise in pH value results in a decrease in the mobility of cationic and an increased mobility of anionic elements. In alkaline pH milieu however the mobility of both cationic and anionic elements tends to increase due to an increased solubility of metal-organic, hydroxide- and carbonate complexes (Lewandowski et al. 1997). A change in redox potential can temporarily increase the solubility of trace elements by e.g. destabilizing oxides in which trace elements were bound. Additionally to its physicochemical properties the composition of the percolation water influences the mobility of trace elements. The effectiveness of the ionic strength of the percolation water e.g. is not only dependent on its strength itself, but also on the com-

position of the background electrolyte (Harter and Naidu 2001). Cationic elements of the background electrolyte, such as Ca, can compete for binding sites at the soil solid phase. E.g. sorption of trace element cations in the presence of Ca ions is lower than in the presence of Na ions (Harter and Naidu 2001). Next to inorganic components, dissolved organic carbon (DOC) in the percolation water acts as a complexing agent. The effectiveness of DOC to build stable complexes with trace elements depends on the dissociation constants of the participating organic acid. Dissociation constants of DOC show a large variety depending on the quality of organic acid, and thus the influence of DOC on the trace element mobility may vary significantly (Harter and Naidu 2001). In addition to complexing agents the total amount of trace elements in percolation water and soil affects equilibrium. In high metal loading rates (< 500 mmol/g) the soils capacity to adsorb further trace elements is limited. Whereas, for low loading rates (< 0.006 mmol/l) when just specific sorption sites are addressed, most ions added will be adsorbed by the soil (Naidu et al. 1994 in: Harter and Naidu 2001). The soil solid phase affects the mobility of trace elements by the quantity and quality of binding sites it offers. Oxides and hydroxides of e.g. Al, Mn and Fe as well as clay minerals and organic carbon contribute binding sites (Lewandowski et al. 1997).

In low concentration levels, in which no competition is present for binding surfaces, the relation between adsorbed and dissolved trace element concentrations follows a simple log-linear function. The Freundlich equation

$$S = K_f \times C^m \quad (1)$$

in which S represents the solid phase concentration [$\mu\text{g}/\text{kg}$], K_f the Freundlich coefficient, C the soluble concentration of the trace element [$\mu\text{g}/\text{l}$] and m the Freundlich exponent, describes the relationship between adsorbed and dissolved trace element concentrations in the soil. Site specific sorption isotherms based on Freundlich equations form part of leaching models to predict trace element transport in the unsaturated zone of the soil in percolation water prognosis (e.g. Finke and Wösten 1996, Altfelder et al. 2007 or Beyer et al. 2009). Extended Freundlich isotherms relate the solid solution partition of trace elements to physicochemical soil properties governing the soil's sorption capacity. These so-called pedotransfer functions (PTF) thereby achieve a broader applicability (van der Zee and van Riemsdijk 1987, Streck 1993, Horn et al. 2003, Römkens et al. 2004, Groenenberg 2011). In transport predictions considering physicochemical and hydrological soil properties the variability of predicted solute concentrations mainly depends on the variability of physicochemical soil prop-

erties (Finke and Wösten 1996). For this reason, the uncertainty analysis in this study focuses on the uncertainty and variability of physicochemical soil properties.

1.2 Sources of Uncertainty

Uncertainty accompanying an estimate of e.g. trace element concentrations in percolation water at the transition zone can stem from various sources. Generally, sources of uncertainty can be differentiated between knowledge or informational uncertainty and natural variability (Figure 3; Keller et al. 2002, Loucks et al. 2005).

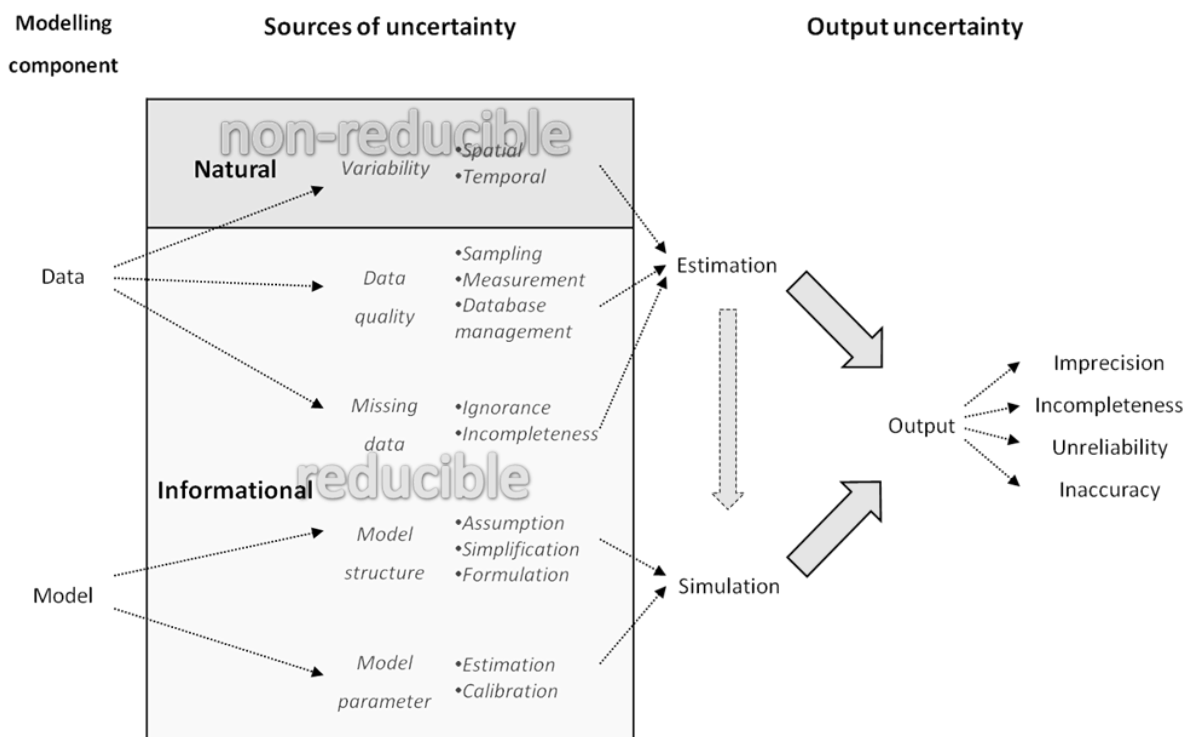


Figure 3: Sources of uncertainty (Wu et al. 2006, supplemented and amended)

Natural variability as a property of nature cannot be reduced while informational uncertainty can to some extent be counteracted by increased sampling or measurement efforts (Frey and Burmaster 1999). Figure 3 shows how sources of natural uncertainty and informational uncertainty can affect the uncertainty of estimates or simulations and thus lead to imprecision, incompleteness, inaccuracy or unreliability of outputs. Precision can be affected by informational uncertainty and natural variability. Accuracy on the other hand is only a product of informational uncertainty, because natural variability is a property of nature.

1.2.1 Natural variability

The natural heterogeneity of soils increases the variance of the data. An unbiased accurate central estimation (e.g. mean or median) of data with a large variability range has little significance, because it merely shows that on average the answer will be correct. It remains uncertain whether a single measurement, estimate or prediction correctly characterizes the typical trace element concentration in the percolation water of this site.

Soil properties and trace element concentrations in the soil can be variable in space or time. Amery et al. 2008, for example, found a 7-fold variation of Cu concentrations within a 5-month period mainly due to variations in DOC concentrations. In lysimeter studies, Bielert (1999) detected that the concentrations of As, Cd, Cr, Cu Ni, Mo, Sb, Sn, Pb and Zn were variable in time and that As, Cd, Cr, Ni, Mo and Sb displayed a weak trend for lower concentrations with higher percolation water rates. However, temporal variability is usually not taken into account in exploratory investigations. Thus, for the scope of this study the focus is on the effects of spatial variability on uncertainty in risk assessment of trace element concentrations in the soil groundwater pathway.

Although spatial variability often increases with greater distance (Dahiya et al. 1984, Spijker et al. 2005), high levels of variability can also be found within the small distances ($\approx 10^2$ m) of the field scale (Biggar and Nielsen 1976, Garten et al. 2007, Altfelder et al. 2007, Heredia and Cirelli 2009).

1.2.2 Informational uncertainty

Informational uncertainty results from lack of knowledge (Frey and Burmaster 1999). Informational uncertainty can be due to uncertain data quality, e.g. measurement errors or incomplete data, or to uncertain model structure and parameters. Uncertainty in model structure is the result of simplifications, assumptions or errors in the formulation of the model. Model uncertainty can also result from uncertainty in model parameters produced in the course of model fitting. For the problem of trace elements percolating from soils to groundwater, it is important to recognize that the processes forming the soil are physical and chemical and obey physicochemical laws in a highly non-linear way (Webster 2000). Technically, all variations in trace element concentrations in the percolation water are deterministic in the sense that they are a result of the natural variability of soil characteristics. However the sensitivity of e.g. sorption or desorption processes to small variations in mineralogy pro-

duces some random error, which in turn leads to undeterminable variations in the dissolved trace element concentrations. Random error causes stochastic uncertainty leading to imprecision, while uncertainty in model structure (leading the model to incorrectly reproduce the process in question) causes deterministic uncertainty (McBratney 1992), which leads to inaccuracy.

Confidence intervals characterize the interval in which the true value of an unknown parameter lies within a preset probability. Confidence intervals are a measure of stochastic uncertainty. Natural variability, like missing data and measurement uncertainty, affects the width of confidence intervals because the chance of collecting a sample which does not correctly characterize the studied environment increases with greater variability in the trace element concentrations (Bolker 2008).

Bias is the expected deviation of the estimated result from the true result and leads to inaccuracy (Bolker 2008). Bias due to model error is a typical source of deterministic and thus of informational uncertainty. The pedotransfer function (PTF) used to predict an exchangeable solid phase trace element concentration is derived from the data of soil samples collected on a national scale. Model error may e.g. result from the fact that site-specific and sorption-relevant soil properties are not relevant on a national scale and are thus not included in the PTF (Heidkamp 2005).

1.3 Objectives and outline

The objective of this study is to analyze and quantify sources of uncertainty in the context of risk assessment for current or future risk for trace elements in the soil groundwater pathway based on analysis of soil material or percolation water. A special focus lies on spatial variability as a source of uncertainty, because as a property of nature it is not reducible. Knowledge of this is of key importance in order to find a balance between economic feasibility and scientific precision when planning and evaluating risk assessments. When the level of informational uncertainty is lower than the uncertainty due to natural variability, the impact of further improvements to reduce informational uncertainty - such as additional sampling or model calibration efforts - will be ineffective.

As stated earlier, spatial variability of physicochemical soil properties can be substantial even within field scale distances and leads to high spatial variability of trace element concentrations in percolation water. The hypothesis may thus be advanced that uncertainty in the risk

assessment of trace elements in the soil groundwater pathway can predominantly be attributed to the spatial variability of physicochemical soil properties.

Uncertainty will be studied with reference to three examples with an increasing volume of sources of uncertainty. In the first example (Chapter 2), uncertainty in risk assessment is studied for the current risk in groundwater contamination. Risk assessment is based on trace element concentrations in percolation water sampled in situ at the transition from unsaturated to saturated zone in the soil. Only soils in which the topmost groundwater body is located in unconsolidated parent material have been taken into consideration. The samples originate from sites which are representative for soils of the Northern German Lowlands in terms of parent material and land use. Because it may be assumed that trace element concentrations in the in situ percolation water represent the true in situ concentration, the predominant source of uncertainty will presumably be spatial variability. The focus thus lies on the effect of spatial variability of soil properties on the variability of trace element concentrations in percolation water. The study analyzes the sources of spatial variability and the effect of spatial variability and stochastic uncertainty on the significance of field (10^2 m) and regional ($> 10^5$ m) scale statistical estimates. The uncertainty of statistical estimates is quantified by nonparametric bootstrap confidence intervals. The effect of regional scale variability on the influence exerted by spatial variability on the representativeness of background values (quantified by percentiles of background concentrations) is studied for trace elements in the percolation water. In the field scale, the effect of spatial variability on the applicability of thresholds is examined. The question to be answered is by how much a median concentration needs to exceed or fall short of a threshold when a one-sided uncertainty of 10% is acceptable.

In Chapter 3, the uncertainty in risk assessment of the current risk for groundwater contamination is again in question. However in contrast to the example used in Chapter 2, the assessment of contamination risk is now based on the leaching behaviour of the solid phase of the soil estimated by batch extraction. In order to quantify the uncertainty, the resulting imprecision or inaccuracy of the batch extraction of the trace element concentrations measured in percolation water collected in situ are compared with trace element concentrations in two different kinds of batch extracts. One extraction method is the aforementioned aqueous batch extract with a liquid solid ratio of 2 l/kg. The second method is an aqueous batch extract with a liquid solid ratio of 5 l/kg with adjusted ionic strength. The latter method was

used to derive the general-purpose PTF mentioned above (Utermann et al. 2005). The uncertainty resulting from systematic changes in the physicochemical properties due to the batch extraction method is assessed by regression analysis. Confidence intervals constructed from standard deviation of the residuals are used to quantify the stochastic uncertainty of a single prediction. In addition to the spatial variability considered in Chapter 2, the uncertainty of data quality is also considered in this chapter.

In Chapter 4 the uncertainty of risk assessment is examined for future risk in groundwater contamination. In transport predictions concerning physicochemical and hydrological soil properties the variability of predicted solute concentrations primarily depends on the variability of physicochemical soil properties (Finke and Wösten 1996). In the uncertainty assessment undertaken, the main focus lies on the uncertainty of sorption isotherms as the model component predicting the sorption capacity of the soil. In this chapter, the field scale variability of sorption-relevant soil properties and trace element concentrations together with and their influence on the uncertainty of PTF predictions, is assessed. Two example sites are chosen with different soil type and texture, each in one or more properties at the edge of the validity range of the PTFs in question. The aim is to quantify sources of uncertainty. Due consideration is given to uncertainty resulting from imprecision in parameterization of the sorption isotherms, spatial variability of input variables, measurement uncertainty and stochastic uncertainty. In addition to spatial variability, this chapter additionally analyzes the uncertainty of model structure and model parameters. No consideration is given to the uncertainty of data quality.

Chapter 5 offers a comprehensive discussion of the main results found in the preceding chapters and is followed by the conclusions outlined in Chapter 6.

2 Application of groundwater thresholds for trace elements on percolation water -A case study on percolation water from Northern German Lowlands-¹

2.1 Abstract

The German insignificance thresholds (GFS) for groundwater, derived with an added risk approach will soon be adopted as trigger values for percolation water entering groundwater. The physicochemical properties of the vadose zone differ considerably from those of groundwater, which may lead to difficulties in the applicability of groundwater derived GFS on percolation water. To test the applicability of the GFS on percolation water with regard to the concentration level and the field scale variability, 46 sites in Northern Germany were sampled, including arable land, grassland and forest, situated on three spatially-dominant parent materials, sand, glacial loam and loess. Concentrations of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn and F were analyzed in percolation water from the transition between the unsaturated to the saturated zone. We compared median and 90th percentile values of the background concentrations with the GFS. In more than 10% of all samples, background concentrations of either Cd, Co, Ni, V or Zn exceeded the GFS. We evaluated the applicability of the GFS on field scale medians of background concentrations taking field scale inter quartile distance and the bootstrap percentile confidence interval of the field scale median of trace element background concentrations into consideration. Statements about exceedance or nonexceedance of GFS values could only be made with acceptable statistical uncertainty ($\alpha \leq 0.1$) when operational median concentrations were about 1/3 higher or lower than the corresponding GFS.

Keywords: background concentrations; trace elements in percolation water; percentile; bootstrap percentile confidence interval; field scale spatial variability

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2.2 Introduction

In Germany, juvenile spring- and groundwater resources satisfy more than 70% of the demand for drinking water (Federal Statistical Office 2007). Traditionally, groundwater quality has been monitored at regular intervals. Because groundwater in Germany is mostly recharged by percolation water, monitoring percolation water quality in addition to groundwater quality is important to the maintenance of good groundwater quality. Consequently, the German soil protection and contaminated site ordinance (BBodSchV 1999) gives thresholds for the vadose zone soil groundwater pathway. In the course of efforts toward a framework directive for soil, waste and water legislation these values will soon be updated and harmonized with insignificance thresholds derived for the groundwater.

The insignificance thresholds for trace elements in groundwater have been derived by an added risk approach. To avoid stigmatizing pristine (i.e. unaffected by anthropogenic activities) water as polluted, within this approach, background values of trace elements characterizing the groundwater in Germany were added to the Predicted No Effect Concentration (PNEC). The basic values were calculated as area-weighted average from 90th percentiles of 15 hydrogeological units in Germany (LAWA 2004). Thus, these thresholds reflect the situation in the groundwater.

The physicochemical conditions in the vadose zone differ considerably from those in groundwater. Consequently, we hypothesize that there may be a discrepancy between background trace element concentrations in the percolation water and those in the groundwater and thus in the applicability of the insignificance thresholds from the groundwater for the percolation water. This motivated us to compile a database with background concentrations in the percolation water of soils from Northern Germany regarding trace elements for which threshold values exist (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn and F) and compare them to their corresponding insignificance threshold (GFS).

Two important issues concerning the practical applicability of thresholds in the percolation water are of interest in this study. The first aspect is the concentration level of a threshold; it should be in the same order of magnitude of the actual background concentration level in order to be applicable. The second aspect we are interested in, regarding the applicability of insignificance thresholds, concerns the spatial variability. Percolation water quality is usually assessed for *areas* of potential concern and soil and percolation water properties are spatially variable. The variability affects the statistical uncertainty and thus the ability to state

with acceptable statistical uncertainty whether for a given area and time a threshold is exceeded or not.

The term “background concentration” as employed in this study is the concentration of a substance in percolation water resulting from the geological situation and from ubiquitous diffuse inputs at a given site. The background concentrations will be presented as “background values” in the form of the median and 90th percentile. The median represents the central tendency of the background concentrations in a given population, whereas the 90th percentile acts as a surrogate representative for the maximum background concentration. With this approach we aim to avoid classifying statistics estimated from elevated trace element concentrations from possibly contaminated sites as background values.

Trace elements in the percolation water can originate from the parent material, the atmosphere or direct input. Natural atmospheric sources of trace elements include volcanic ashes and eolian dusts. Additionally, in densely populated and highly industrialized countries such as Germany, even in rural areas anthropogenic sources for trace elements in percolation water cannot be ruled out. Anthropogenic sources for atmospheric depositions include aerosol emissions resulting from industrial plants, cars, metallurgical industries or the generation of energy from fossil resources (Adriano 2001). Ubiquitous direct input of trace elements can result from the use of soil amendments, such as fertilizers, limes and animal manure, as well as pesticides, herbicides or insecticides.

Soil properties affecting the solubility of trace element change depending on land use. On arable land the sorption capacity and contents of organic carbon will be increased and pH values will be set to 5-6 in order to achieve best possible plant nutrition. Long term land use as forest, especially under conifers, will result in increasing acidification of soils. Soils which are too wet for arable land are often used as grassland. High biomass production and incomplete decomposition on such sites will increase DOC concentrations in the percolation water and thus increase the mobility of trace elements with an affinity for metal-organic complexes. Land use effects on the concentrations of trace elements will be most visible in the percolation water from soils generated from parent materials with low sorption and buffer capacities, such as sand.

Most anthropogenic sources of trace elements enter the soil at the surface. Soils with relatively large amounts of organic material, such as topsoils, have particularly large partition coefficients for trace elements (Peijnenburg et al. 2001, Grathwohl and Susset 2009). Trace

elements deposited onto the soil surface accumulate in the topsoil, and unless the soils are overloaded, these elements barely translocate downward in the soil profile (Heredia and Cirelli 2009). Thus, the chances of finding concentration levels of trace elements in the percolation water that can be considered background increase with the vertical distance from the soil surface.

Properties of soil and percolation water as well as trace element concentrations are variable in space and time. Amery et al. 2008, for example, found 7 fold variation of Cu concentrations within a 5 month period mainly due to variations in DOC concentrations. Bielert (1999) found in lysimeter studies that the concentrations of As, Cd, Cr, Cu Ni, Mo, Sb, Sn, Pb and Zn were variable in time and that As, Cd, Cr, Ni, Mo and Sb showed a weak trend for lower concentrations with higher percolation water rates. However, for exploratory investigations in which GFS are applied, temporal variability is usually not considered. Thus, for the scope of this project we will focus on the effects of spatial variability on the applicability of GFS on trace element concentrations in percolation water.

The spatial heterogeneity generally tends to increase with scale (Dahiya et al. 1984, Spijker et al. 2005). However, Biggar and Nielsen (1976) reported great horizontal and vertical variability of soil leaching characteristics at the field (10^2 m) and profile (10^{-1} m) scales. Garten et al. (2007) discovered that the spatial variability of soil properties, such as mineral associated organic carbon, was as variable at small scales (1 - 10 m) as it was at scales of 50 - 500 m. Heredia and Cirelli (2009) reported large profile scale variability of Ni in the pore water. Spijker et al. (2005) detected the largest component of variance in As, Cd, Cu, Pb, Sb and Zn concentrations in soils within 300 m and Altfelder et al. (2007) found field scale (< 100 m) variability in trace element concentrations of one to two orders of magnitude. They reported that 70% of the variance in the concentration of potentially exchangeable trace elements in soils could be attributed to field scale variance (Altfelder et al. 2007). Thus, we assume that the field scale variability of trace element concentrations in the percolation water will be considerably high.

Our first objective in this paper is to evaluate whether the insignificance thresholds GFS are suitable to be applied on percolation water samples in Germany with regard to their concentration level. Therefore we compiled a database with background concentrations of trace elements in the percolation water of the transition between the unsaturated and the saturated zone in the soil representative for the spatially dominating parent materials and land

uses. In order to avoid variations in the trace element concentrations resulting from differences in analytical methods, sampling technique and/or sampling devices, the database is uniform in terms of sampling and analytical methods. Due to limitations in the sampling technique the investigation was restricted to percolation water in unconsolidated sediments in the Northern German lowlands. We assume that due to physicochemical differences between the groundwater and the percolation water background concentrations of trace elements in a large proportion of the percolation water samples will exceed their corresponding insignificance threshold.

The second objective is to evaluate the applicability of insignificance thresholds for groundwater on percolation water on the field scale with regard to the spatial variability of trace element concentrations in the percolation water. We are especially interested in the effect of the spatial variability on the statistical power of field scale central measures (e.g. median). In order to evaluate the field scale applicability of the insignificance values, we compared the typical field scale uncertainty given as the bootstrap confidence interval for the median from 10 samples per site to the insignificance threshold.

2.3 Materials and Methods

2.3.1 Site selection and description

The sampling sites were representative for Northern Germany in terms of parent material (BAG 1000 and BÜK 1000), depth of the groundwater table (HÜK 200), and annual percolation water rate (BMU 2003), predominant forms of land use, (which are arable land, grassland and forest according to CORINE Land Cover 2000), atmospheric background depositions (excluding areas downwind of industrial and urban areas) and total i.e. aqua regia extractable background contents (Supplemental Table S 1 in the supplementary information) of trace elements in soil (LABO 2003). The number of sites sampled for each of the four parent material- land use units represents the spatial distribution of parent material and land use in Northern Germany (Figure 4). (i) sand/arable land (SA/A; 15 sites, 145 samples), (ii) sand/forest (SA/F; 11 sites, 99 samples), (iii) sand/grassland (SA/G; 5 sites, 49 samples) and (iv) glacial loam or loess/arable land (LL/A; 15 sites, 125 samples). Table 1 shows some physicochemical properties of the soils and the percolation water.

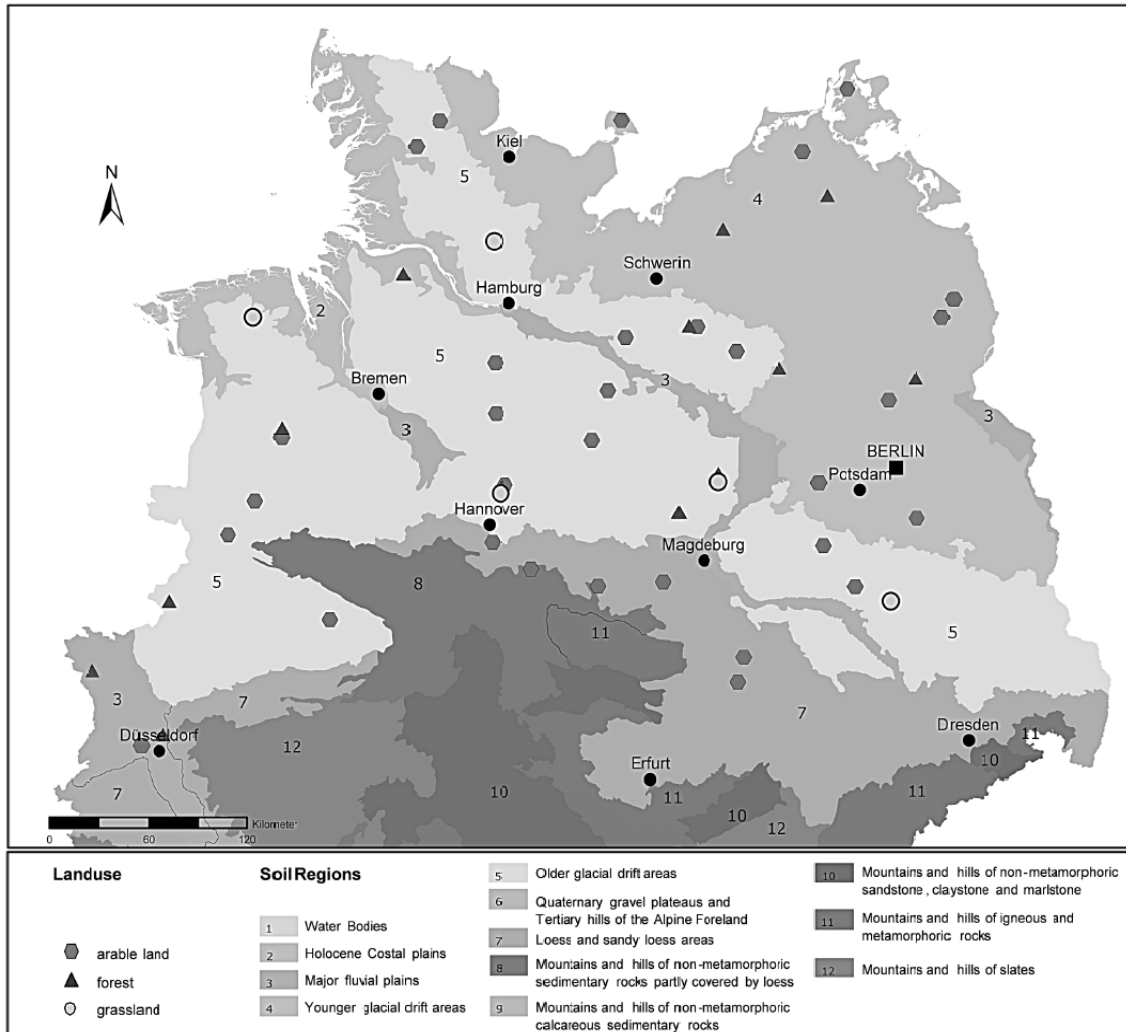


Figure 4: Location of sampling sites and soil regions in Northern Germany

To evaluate the temporal variability of trace element concentrations we sampled one site one time each in the years 2001, 2003 and 2008 (Supplemental Figure S 1 in the supplement). The temporal variability was often smaller than spatial variability. Keeping in mind that for exploratory investigations of site characteristic trace element concentrations the temporal variability is usually not considered, each site was sampled once during the course of the project and temporal variability was thus not investigated any further in the course of this study.

Spatial variability was investigated at field and regional scale. Accordingly multiple samples were drawn on each site with a standard sampling design of 10 samples per site arranged along a linear transect with a distance from point to point of 10 m.

The depth directly above the groundwater table at the transition from the unsaturated to the saturated zone was the best location for sampling percolation water, because the chance

of finding untainted percolation water increases with increasing distance from the topsoil.

Percolation water can be distinguished from groundwater by its hydrostatic pressure.

Table 1: Some physicochemical properties of the soil and of the percolation water, both taken from the transition from the unsaturated to the saturated zone in soils of different parent material and different land use. Cation exchange capacity (CEC), organic carbon (C_{org}) and oxalate soluble Fe (Fe_{ox}) and Mn (Mn_{ox}) were analyzed in the soil at the sampling depth, pH, electrical conductivity EC, NO_3 and dissolved organic carbon (DOC) in percolation water (SA/A sand/arable land, SA/F sand/ forest, SA/G sand/grassland, LL/A loess or glacial loam/arable land)

		1 st quartile	median	3 rd quartile
CEC [mmol _c /kg]	SA/A	4	9.4	16
	SA/F	7.1	9.1	14
	SA/G	7.9	11	15
	LL/A	14	33	80
C_{org} [mass%]	SA/A	0.03	0.06	0.11
	SA/F	0.03	0.05	0.1
	SA/G	0.09	0.15	0.34
	LL/A	0.1	0.23	0.53
Fe_{ox} [mg/kg]	SA/A	98	176	332
	SA/F	152	299	438
	SA/G	39	88	252
	LL/A	219	432	690
Mn_{ox} [mg/kg]	SA/A	<6.0	<6.0	<6.0
	SA/F	<6.0	<6.0	17
	SA/G	<6.0	<6.0	<6.0
	LL/A	32	96	174
pH	SA/A	4.6	5.3	6.4
	SA/F	3.9	4.2	5.5
	SA/G	5.1	6.4	7.5
	LL/A	6.8	7.2	7.3
EC [μ S/cm]	SA/A	232	382	530
	SA/F	183	255	395
	SA/G	129	270	1102
	LL/A	725	1170	1654
NO_3 [mg/l]	SA/A	46	77	142
	SA/F	3.1	5.5	23
	SA/G	8.7	17	68
	LL/A	63	109	136
DOC [mg/l]	SA/A	4.4	9.1	20.3
	SA/F	3.3	6	9.6
	SA/G	21.9	26.4	32.8
	LL/A	3.3	4.1	5.8

In theory in the percolation water the hydrostatic pressure is lower than the atmospheric pressure and in the groundwater it is higher than the atmospheric pressure. Because of technical advantages (such as better hydraulic conductivity), percolation water was sampled from the topmost 0 - 10 cm of the topmost groundwater instead from the transition zone. It was made sure that the parent material, soil texture and redox conditions were the same

both in the transition zone and in the zone of the topmost groundwater level. Sampling points were restricted to sites without inclination and without any form of lateral or upward groundwater movement and were at least 100 m away from the nearest field or forest margin. On every sampling point one sample of percolation water and one sample of soil material were taken at the exact same depth. On every site one soil sample from the topsoil was taken.

2.3.2 Sampling technique

The sampling device was a low-sorption suction cup with 0.45 μm nylon membrane, attached to internal fluorinated ethylene propylene (FEP) sample collector connected via FEP sampling tube. To install the sampling device, a borehole was drilled 10 - 15 cm above the intended sampling depth. The borehole was then cleaned with an industrial vacuum cleaner attached to a plastic tube to avoid contamination due to soil material fallen into the borehole from upper horizons. The last 10 - 15 cm of water-saturated soil was excavated by applying negative pressure to a Plexiglas tube. The same method was used to sample soil from this depth. The water-saturated soil was transported in polyethylene bags, subsequently dried at 40°C, sifted < 2 mm in a nylon sieve and stored dry in a polystyrene container with polyethylene terephthalate lid. Once the sampling device was installed, a suction of 80 kPa was applied to the suction cup. The water sample was exposed only to low sorption material and was stored in the dark at the prevailing soil temperature in the FEP shaft cavity until withdrawal. At the end of the sampling period (5 to 20 h), the shaft cavity containing the sample was withdrawn from the sampling device, and the sample (approximately 200 ml) was prepared for analysis.

2.3.3 Percolation water analysis

Immediately after its removal from the sampling device, four aliquots of the sample were prepared, (i) one aliquot to analyze pH, temperature and electrical conductivity on site with a multi-parameter instrument equipped with a conductivity cell, a pH-electrode and a temperature probe. After pH and electrical conductivity measurements, this aliquot was used to analyze alkalinity by Gran-titration (Gran 1950). (ii) The second aliquot was stored in a glass bottle and used to analyze the dissolved organic carbon (DOC). Inorganic carbon was first purged from the acidified sample. The remaining organic carbon (“non-purgeable”) was oxidized by oxygen. The amount of formed CO_2 was quantified using an IR-detection device

(high TOCII elemental). (iii) The third aliquot was stored in a polyethylene (PE) bottle, which was completely filled, and used to analyze the main cations and anions with inductively coupled plasma-optical emission spectrometry (ICP-OES; Spectro Cirrus CCD) and ion chromatography (IC, Dionex IC3000, column: AS19). (iv) The fourth aliquot was stored in a PE bottle and stabilized by the addition of nitric acid (65% m/m, suprapur) to obtain a final acid concentration of 0.14 mol/l. This aliquot was used to analyze trace element concentrations using magnetic sector inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Fisher Scientific, ELEMENT). The quality of the trace element concentration analysis was checked by analyzing the international reference materials for trace elements in water SLRS-4 in parallel. Deviations from the certified values were generally less than 10%. Finally, the results of the different analytical methods were combined and checked by calculating the ionic charge balance; the errors of the charge balance were generally below 10%.

2.3.4 Soil analysis

The content of organic carbon (C_{org}) was calculated as the difference between total carbon, analyzed by high temperature combustion and subsequent gas analysis (elementar vario Max CNS) and carbonate carbon, analyzed volumetrically via calcimeter (Scheibler unit). The cation exchange capacity (CEC) was measured by percolating the soil with 0.1 mol/l $BaCl_2$ solution and subsequently analyzing the cation concentrations in the percolate in an ICP-OES. The sesquioxide bound Fe and Mn contents were estimated by extracting 1 g dry soil with 50 ml 0.2 mol/l ammonium-oxalate-solution for 2 h omitting ultraviolet radiation and shaking at 20 rpm in an end-over-end shaker. Na_2 -EDTA-extractable trace element concentrations were measured in an extract made of 4 g soil and 40 ml 0.025 mol/l Na_2 -EDTA-solution which was homogenized for 24 h, centrifuged and filtered $< 0.45 \mu m$. Concentrations $< LOQ$ have been excluded. F was not measured in Na_2 -EDTA-extracts. For aqua-regia extraction 3 g of ground soil material were mixed with 21 ml HCl and 7 ml HNO_3 in 250 ml digestion tubes and left over night. The mixture was then slowly ($2^\circ C/min$) heated to $180^\circ C$ in a complete Behr digestion apparatus. This temperature was held for 2 h. After cooling, the extract was filtered through pleated filters. Element concentrations were analyzed in ICP-OES, ICP-MS and IC.

Modifications of analytical methods within the measurement period of 2001 to 2008 resulted in changing the limits of quantification (Table 2). The limit of quantification refers to the concentration above which concentrations can be quantified with a maximum level of

relative uncertainty (Funk et al. 2005); it was calculated by multiplying the standard deviation of the detection limit by ten. Element concentrations below the limit of quantification (LOQ) were considered with the value of the limit.

Table 2: Range of limits of quantification and insignificance thresholds GFS (LAWA 2004)

	limits of quantification	insignificance threshold GFS
	[µg/l]	
As	0.1 - 3	10
Ba	0.04	340
Cd	0.004 - 0.1	0.5
Co	0.01 - 0.1	8
Cr	0.08 - 0.9	7
Cu	0.3 - 0.5	14
Mo	0.003 - 0.1	35
Ni	0.03 - 0.1	14
Pb	0.02 - 0.5	7
Sb	0.001 - 0.01	5
Sn	0.02 - 0.2	40
V	0.01 - 0.1	4
Zn	0.02 - 7	58
F	10	750

2.3.5 Statistics

The data were \log_{10} -transformed and then tested for extremes using a box plot analysis (SPSS Inc. 2009). Less than 3% of the data were excluded because they were identified as extreme values. Extreme values are values smaller than $Q_1 - 3(Q_3 - Q_1)$ and values larger than $Q_3 + 3(Q_3 - Q_1)$, where Q_1 is the first quartile and Q_3 is the third quartile of a distribution (SPSS Inc. 2009).

One site with sandy soils under forest was excluded entirely from the database because of its low pH (< 3). The low pH at this particular site was attributed to anthropogenic industrial emissions, which disqualified it for the purposes of estimating natural background values.

Due to difficult sampling conditions, such as low conductivity in loamy soils, or substrate with e.g. high contents of gravel, that made drilling and sampling difficult, it was not always possible to gain a full collection of 10 samples. To represent every site equally, the data points were weighted to ensure that all sites had the statistical weight of ten samples. One

site was excluded from the database because less than five samples could be taken. In total, the database consisted of 418 samples from 46 sites.

The median and 90th percentile values were calculated using the weighted average method (Cleff 2008). If more than 50% of the values were below the limit of quantification, it was not possible to characterize the samples correctly by percentiles. Thus, no percentiles could be calculated for Se.

Confidence intervals were calculated as bias-corrected and accelerated (BCa) nonparametric bootstrap percentile confidence intervals (CI) with one-tailed $\alpha = 0.1$ (Efron and Tibshirani 1993 and Davidson and Hinkley 1997) (For further information please refer to the supplementary information). The CI were calculated with package “boot” in the statistical software program R (R Development Core Team 2011), and are displayed as error margins around the median and 90th percentile bars (Figure 5). The limits of the CI can be found in Table 3.

We analyzed the relation between sorbed (i.e. EDTA-extractable) and dissolved trace element concentrations by stepwise multiple regression analysis. The probability value for entry was 0.05 and for removal it was 0.10. As covariates additional to the EDTA-extractable concentration of trace elements, physicochemical properties of the soil and the percolation water were taken into account.

The spatial variability of trace element concentrations is especially important on a field scale level, because it determines how well a site can be represented by a statistical parameter e.g. the field scale median through a limited number of samples. A typical scenario could be an exploratory investigation on a site trying to assess whether the trigger values for percolation water (in our case the GFS) are likely to be exceeded at the place of assessment (in our case at the transition from the unsaturated to the saturated zone). In such exploratory investigations usually less than ten samples are drawn. We estimated the field scale variability through the IQD (interquartile distance) and the uncertainty of the field scale median with the CI with one-tailed $\alpha = 0.1$.

Statistics were calculated with the software IBM SPSS 19 Statistics or the software program R (R Development Core Team 2011).

2.4 Results and Discussion

The sampling depth for the percolation water and the corresponding soil samples was solely dependent on the groundwater table and varied from site to site between one and six meters below surface. The groundwater level did not depend on the land use. Preliminary stud-

ies showed that trace element concentrations in water samples from actual percolation water (i.e. water from the transition of the unsaturated to the saturated zone, where the hydrostatic pressure usually is smaller than the atmospheric pressure) differed less than 10% from concentrations measured in water samples taken 10 - 15 cm deeper from the first 5 - 10 cm below the groundwater table.

2.4.1 Background concentrations of trace elements in the percolation water

Table 3 shows the median and the 90th percentile of the trace element concentrations together with their upper and lower ($\alpha = 0.1$) nonparametric bootstrap percentile confidence limit. Figure 5 shows the percentiles in relation to their corresponding insignificance threshold GFS.

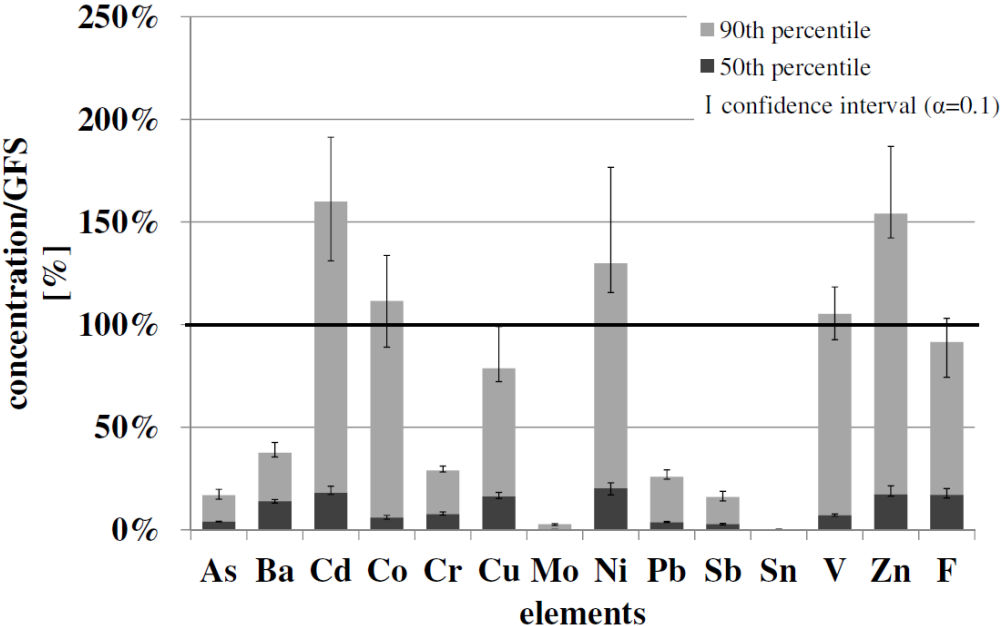


Figure 5: Median and 90th percentile of background trace element concentration in the percolation water in relation to the corresponding German insignificance threshold for trace elements in the groundwater (GFS; $\exists 100\%$) and their upper and lower nonparametric bootstrap percentile confidence limit ($\alpha = 0.1$)

The error bars are ($\alpha = 0.1$) nonparametric bootstrap percentile confidence intervals. The medians of the trace element concentrations were always smaller than 20% of the GFS. The 90th percentiles of Cd, Co, Ni, V and Zn background concentrations were higher than their corresponding insignificance threshold. The upper confidence limit of the 90th percentile of F

exceeded the insignificance threshold and the upper confidence limit of the 90th percentile of Cu concentrations was just below the threshold.

Table 3: Median and 90th percentiles with nonparametric bootstrap percentile confidence intervals (CI) $\alpha = 0.1$ of trace element concentrations [$\mu\text{g/l}$] in percolation water from the transition between unsaturated and saturated zone in the soil

	lower confidence limit	median	upper confidence limit	lower confidence limit	90 th percen- tile	upper confidence limit
As	0.39	0.40	0.43	1.5	1.7	2.1
Ba	44	46	50	121	129	146
Cd	0.086	0.095	0.104	0.67	0.80	0.97
Co	0.42	0.47	0.57	7.1	8.8	11
Cr	0.51	0.56	0.61	2.0	2.1	2.2
Cu	2.2	2.4	2.6	10	12	14
Mo	0.07	0.08	0.10	0.74	0.90	1.06
Ni	2.4	2.9	3.3	16	18	26
Pb	0.249	0.251	0.288	1.7	1.9	2.0
Sb	0.12	0.14	0.16	0.71	0.81	0.94
Sn		≤ 0.04		0.10	0.11	0.14
V	0.26	0.29	0.31	3.8	4.2	4.8
Zn	9	11	12	82	95	109
F	117	129	151	558	681	777

At least 10% of percolation waters yielded background concentrations higher than the insignificance threshold for Cd, Co, Ni, V or Zn. In order to evaluate what kinds of percolation water were prone to yield higher trace element contents, we studied which physicochemical properties were most influential on the mobility of trace elements by multiple stepwise regression analysis (Table 4).

For the elements Cd, Zn, Mo, Pb, Co and Ni the pH-value was the parameter with the highest coefficient of determination. Cd, Co, Ni and Zn become increasingly mobile at decreasing pH values (Ross 1994, Gäbler 1997). Figure 6 shows boxplots of trace elements with affinity toward pH. They have been grouped into sets of percolation water with pH < 4.2 (Fe/Al buffer), pH 4.2 - 6.5 (silica and clay mineral buffer) and pH > 6.5 (carbonate buffer). Percolation water with pH < 4.2 had higher concentrations of Cd, Zn, Pb, Co and Ni and more than 50% of these samples exceeded the insignificance threshold for Cd or Zn. Low pH values were found particularly often in percolation water from forest on sandy soils (Table 1).

Table 4: Model summary of multiple stepwise regression with log₁₀-transformed data (except pH), the independent variables are listed in the order in which they were entered into the model, dependent variable = trace element concentration in percolation water, r² = coefficient of determination

Dependent variable	Independent variables and standardized regression coefficients											r ²	N	
	1st	2nd		3rd		4th		5th		6th				
Cd	pH	-0.66	C _{org}	-0.34	Cd _{EDTA}	0.23	Fe _{ox}	0.15	DOC	0.11			0.63	192
Zn	pH	-0.57	C _{org}	-0.31	Zn _{EDTA}	0.15	DOC	0.15	Fe _{ox}	0.13			0.58	192
Mo	pH	0.70	DOC	0.25	Mo _{EDTA}	0.28	Fe _{ox}	-0.24					0.60	197
Pb	pH	-0.53	DOC	0.43									0.49	367
Co	pH	-0.59	Mn _{ox}	-0.41	Fe _{ox}	0.21	Co _{EDTA}	0.20					0.46	207
Ni	pH	-0.37	Ni _{EDTA}	0.49	C _{org}	-0.41	DOC	0.25	Fe _{ox}	0.15	NO ₃	-0.10	0.50	190
As	DOC	0.23	As _{EDTA}	0.40	pH	0.25	Fe _{ox}	-0.14	Mn _{ox}	-0.14			0.35	197
Cu	DOC	0.70	C _{org}	-0.30	Cu _{EDTA}	0.18	NO ₃	0.16	pH	-0.13	Fe _{ox}	0.11	0.57	190
V	DOC	0.37	Fe _{ox}	-0.32	V _{EDTA}	0.26	Mn _{ox}	-0.20					0.60	199
Cr	DOC	0.48	pH	-0.30									0.33	367
Sb	DOC	0.65	Sb _{EDTA}	0.29	pH	0.26	C _{org}	-0.25					0.65	211
Sn	DOC	0.50	Sn _{EDTA}	-0.30	C _{org}	0.26							0.30	214
Ba	Ba _{EDTA}	0.39	C _{org}	-0.33	Mn _{ox}	0.27	NO ₃	-0.16	pH	0.22			0.31	209

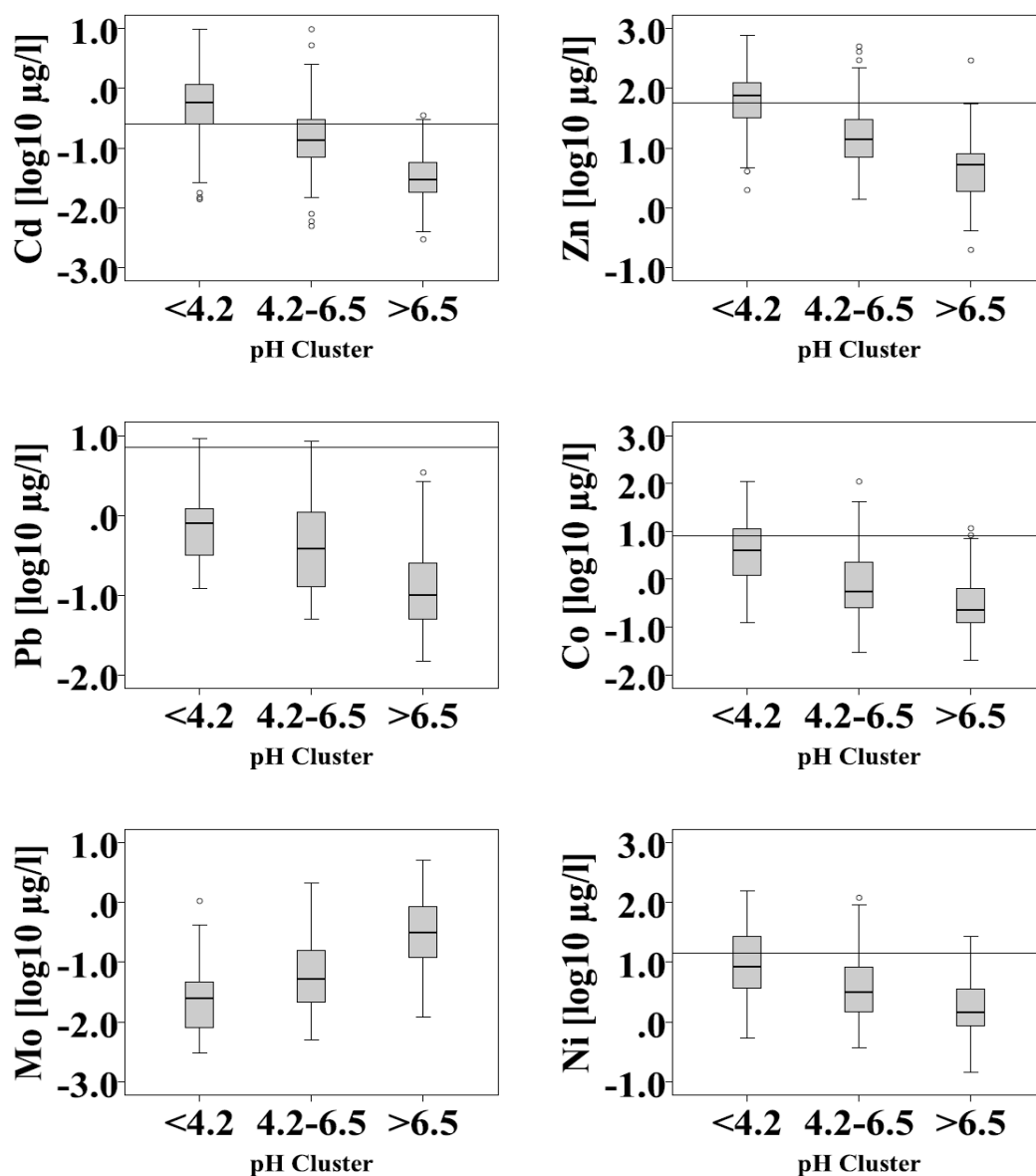


Figure 6: Boxplot diagrams of background concentrations of Zn, Cd, Pb, Co, Mo and Ni in percolation water, sorted into groups of percolation water with pH < 4.2, pH 4.2 - 6.5 and pH > 6.5, solid horizontal lines in the diagram = corresponding German insignificance threshold for trace elements in groundwater (GFS)

In aerobic conditions, Mo is present as MoO_4^{2-} (Takeno 2005). Thus, the mobility of Mo increases with increasing pH values. This relationship was observed in our results (Figure 6). However, the highest Mo concentrations were not found in percolation water with the highest pH values, i.e. from loess and loam. Particularly Fe-oxides have strong sorption capacity for Mo (Adriano 2001). Maybe as a result of the higher contents of Fe-oxides, despite the high pH values of percolation water from parent materials glacial loam or loess used as arable land, Mo mobility was lower in these soils than in percolation water from sandy soils used as grassland.

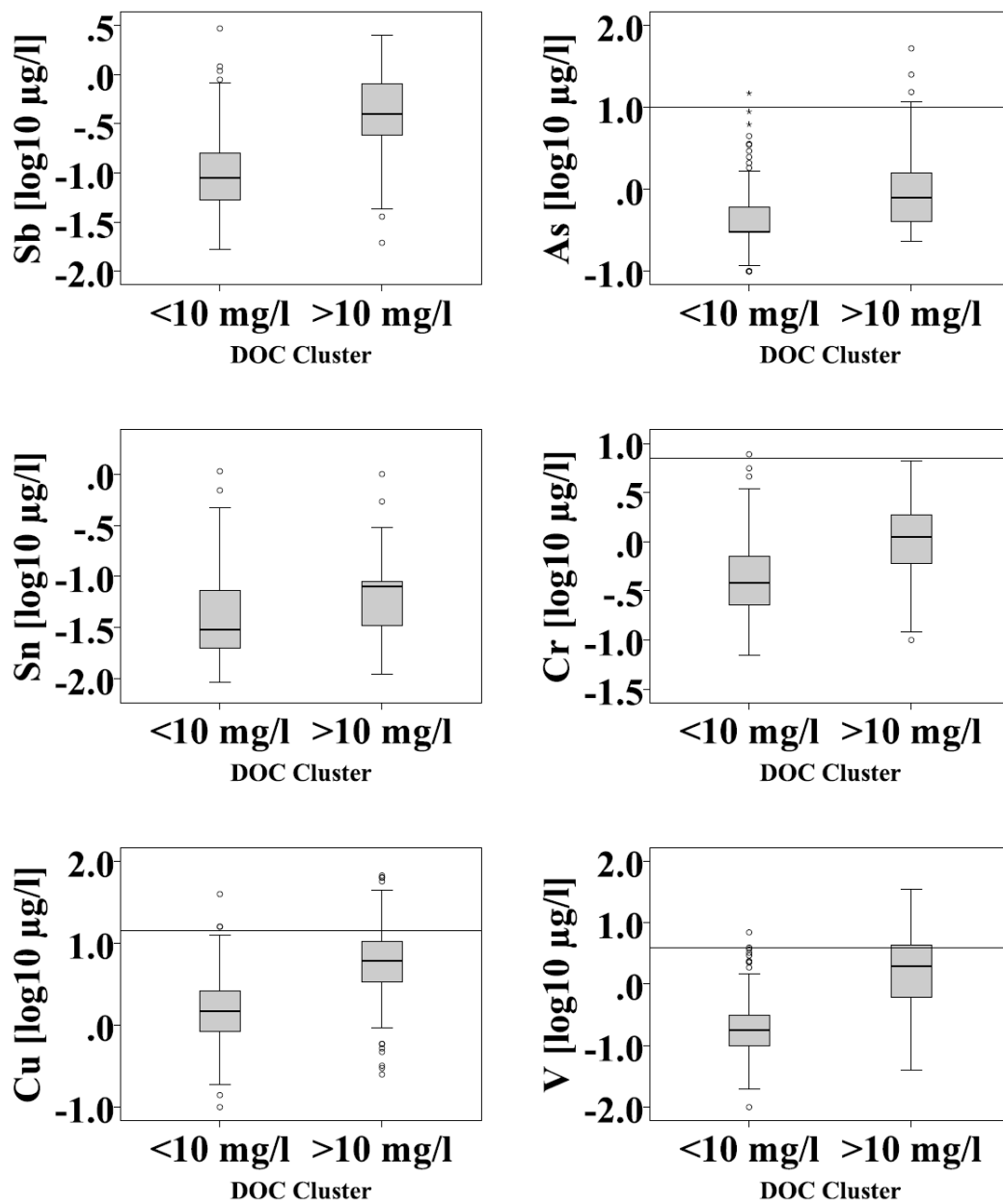


Figure 7: Boxplot diagrams of background concentrations of Sb, As, Sn, Cr, V and Cu in percolation water, sorted into groups of percolation water with DOC concentrations < 10 mg/l and > 10 mg/l, solid horizontal lines in the diagram represent the corresponding German insignificance threshold for trace elements in groundwater (GFS)

The relation between pH and F mobility in soil (not shown) is U-shaped (Fung et al. 1999). Up to pH of 6.5 increasing pH leads to decreasing mobility of F. Above pH 6.5 the mobility of F increases again (Wenzel 1992). This increase explains the elevated background values of F in percolation water from parent materials glacial loam or loess used as arable land.

Pb mobility is primarily related to pH (Adriano 2001). Additionally, Jordan et al. (1997) discovered that Pb solubility was enhanced by DOC when DOC concentrations were higher than

4 mg/l, which is in accordance with the results of our stepwise regression analysis. The mobility of Cr is strongly influenced by the pH (Adriano 2001). In addition, studies on different methods of aqueous extractions showed, that increased DOC-mobilization lead to increased Cr-concentrations in the solution (Godbersen et al. 2011). Kalbitz and Wennrich (1998) report a positive correlation of DOC and Cr in aqueous extracts. Cr also has a high affinity toward Mn-(hydr-)oxides (Adriano 2001, Ross et al. 2001). As a result, the already strong sorption effect of high pH in soil-water-systems in loess or loam, could be enhanced by existing Mn-(hydr-)oxides. Loess and loam soils contained more Mn-(hydr-)oxides than sandy soils (Table 1).

Figure 7 shows that concentrations of Sb, As, Cr, Cu, and V were higher in percolation water with higher (> 10 mg/l) DOC concentrations. In the multiple stepwise regression analysis the concentrations of As, Cu, V, Cr, Sb and Sn in the percolation water showed the strongest relation to the DOC concentrations (Table 4). Due to the low coefficients of determination (r^2 , see Table 4) a sound geochemical interpretation of the obtained data for the elements As, Cr, Sn, and Ba cannot be drawn. Additionally the extremely low solubility of SnO_2 in aqueous solutions resulted in very low Sn concentrations (more than 40% of the percolation water samples yielded concentrations lower than the limit of quantification), which precludes a sound interpretation of Sn.

Cu is known to form complexes with phenolic or carboxylic groups of DOC while stable oxalate complexes have been reported for V at $\text{pH} < 5$, resulting in an increased mobility of these elements (Temminghoff et al. 1998, Wanty and Goldhaber 1992). Gäbler et al. (2009) conclude that V is likely adsorbed by Fe-, Al-, and Mn-(hydr)oxides which comprehends with the negative standardized regression coefficients we found in the multiple stepwise regression analysis. Takahashi et al. (1999) found inhibiting effects of humic acids on kaolinit and silica surfaces likely to be responsible for increased V dissolution. Sb is suspected to compete with humic and especially fulvic acids of DOC for anion binding surfaces such as Mn- or Fe(hydr-)oxides (Weng et al. 2009, Gustafsson 2006 and Groenenberg 2011). Since Sb is mostly present as SbO_3^- its solubility increased as expected with increasing pH-values (Table 4).

The background concentrations of trace element in the percolation water were in the same order of magnitude as the background concentration in the shallow groundwater (0 - 10 m) of the hydrogeological unit "glacial sand and gravel deposits in Northern German Lowlands",

which underlies our percolation water sampling region (Table 5). Nevertheless, the influence of the differences in the physicochemical milieu could be seen in the trace element concentrations. The pH for example was much higher in the groundwater (median = 7.0, Kunkel et al. 2004) and the condition in aquifers of unconsolidated sediments are usually more reductive (Wendland und Kunkel 1999 in Kunkel et al. 2004). Consequently, concentrations of anionic trace elements sensitive to pH and/or redox potential, such as Mo, Sb or Cr were higher in the groundwater than in the percolation water.

Table 5: Median and 90th percentile of trace element concentrations in shallow groundwater (0 - 10 m) from the hydrogeological unit „Glacial Sands and Gravel Deposits in Northern German Lowlands“ (Kunkel et al. 2004)

	As	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Sn	V	Zn	F
	[µg/l]													
<i>Median</i>	1.3	59	0.3	1.4	2.8	3.0	-	5.9	2.0	0.1	-	-	20	100
<i>90th percentile</i>	7.5	180	0.8	10	6.7	10	-	20	6.7	0.05	-	-	238	300

The measured trace element concentrations were well comprehensible, when physicochemical parameters are taken into account. Since we made sure only to include sites that showed no signs of contamination with trace element concentrations in the topsoil or in the soil at the sampling depth (Supplemental Table S 1) also the elevated concentrations in the percolation water were background. Higher background concentrations of pH sensitive elements were often found in percolation water from sandy soil under forest. Consequently, the background concentration of Cd, Ni, Co and Zn in percolation water from sandy soils under forest often exceeded the GFS. Elements which showed a high affinity toward metal-organic complexes or which competed with DOC for binding surfaces were present in higher concentrations in percolation water with high concentrations of DOC. High DOC concentrations were found mostly on sites with grassland on sandy soils. Accordingly, thresholds of DOC sensitive elements such as Cu or V were mostly exceeded in grassland percolation water.

It can be argued whether it is justified to adjust trigger values such as the GFS to the specific existing physicochemical conditions. Under forests for example due to ubiquitous acidification pH values were generally low and in consequence mobility of pH sensitive cationic trace elements was high. Because this is a ubiquitous phenomenon one could allow higher trigger values for sites with generally low pH values. On the other hand one could also argue that it is necessary to raise the pH values, e.g. by liming and thereby lower the background concen-

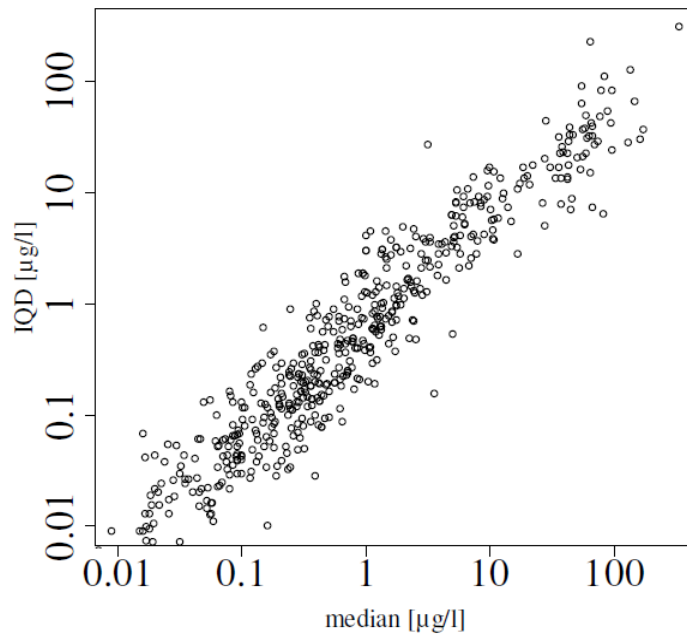
tration of trace elements in the percolation water, because the problem was manmade since the acidification of forest soils was mainly caused by anthropogenic emissions.

2.4.2 Effects of spatial variability on the field scale applicability of German insignificance thresholds on percolation water

Future legislative decisions will apply the GFS as trigger values for percolation water for areas of field scale size. The decisions whether the area is potentially contaminated and should be investigated in further detail are usually based on mean or median concentrations of this area. The uncertainty i.e. the width of the confidence interval of the mean or median strongly depended on the spatial variability. Various authors report that a large proportion of the variability of trace element concentrations can be found within meters (e.g. Altfelder et al. 2007, Heredia and Cirelli 2009 or Spijker et al. 2005).

Figure 8 a) shows that the relation between the median concentration and variability (i.e. IQD) of the measured trace element concentrations on the field scale was linear. Every dot represents the combination of the field scale median and IQD of one element for one site. Supplemental Table S 2 in the supplementary information shows the coefficients of the linear relation between the median concentration and the IQD on a field scale level. In Figure 8 b) the field scale IQD of all elements and sites are plotted against their ($\alpha = 0.1$) CI. They too were linearly related. These relations between the median and the IQD allowed us to estimate the average field scale IQD of any element for a given median (e.g. the GFS value) based on linear regression models (Supplemental Table S 2). This estimated field scale IQD could then be used to estimate the CI ($\alpha = 0.1$) that can be expected for the chosen element at the chosen concentration level.

a)



b)

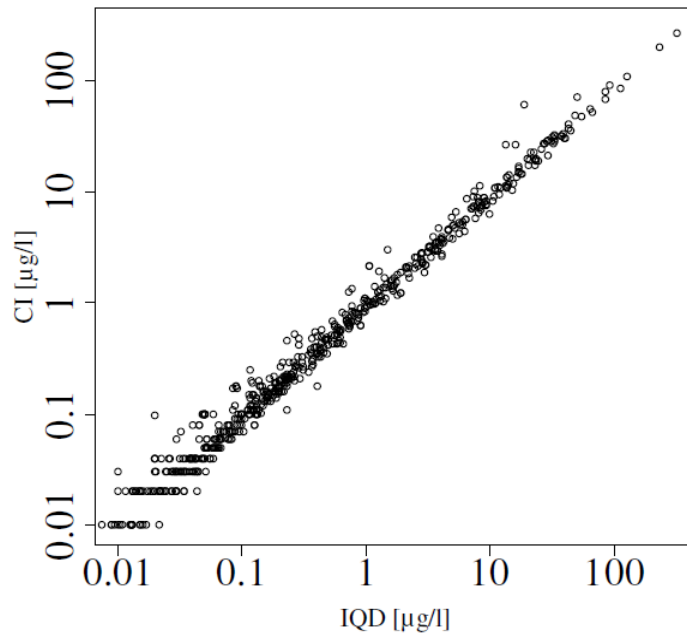


Figure 8: Field scale median plotted against field scale interquartile distance IQD of trace element concentrations in percolation water, field scale IQD plotted against $\alpha = 0.1$ bootstrap percentile confidence interval (CI) of the field scale median of trace element concentrations in percolation water (assumed sample size per site $N = 10$), one dot represents one site and one trace element

Figure 9 shows what kind of uncertainty can be expected if for a given site the median concentration, calculated from $N = 10$ samples, equals the GFS. The width of the CI was closely

connected to the slopes (coefficients b in Supplemental Table S 2) of the equation used to estimate the field scale IQD from the field scale median concentration. Higher b coefficients resulted in wider CI. It was not possible to find plausible explanations based on physico-chemical characteristics for the differences in the regression coefficients for the slope of the different elements.

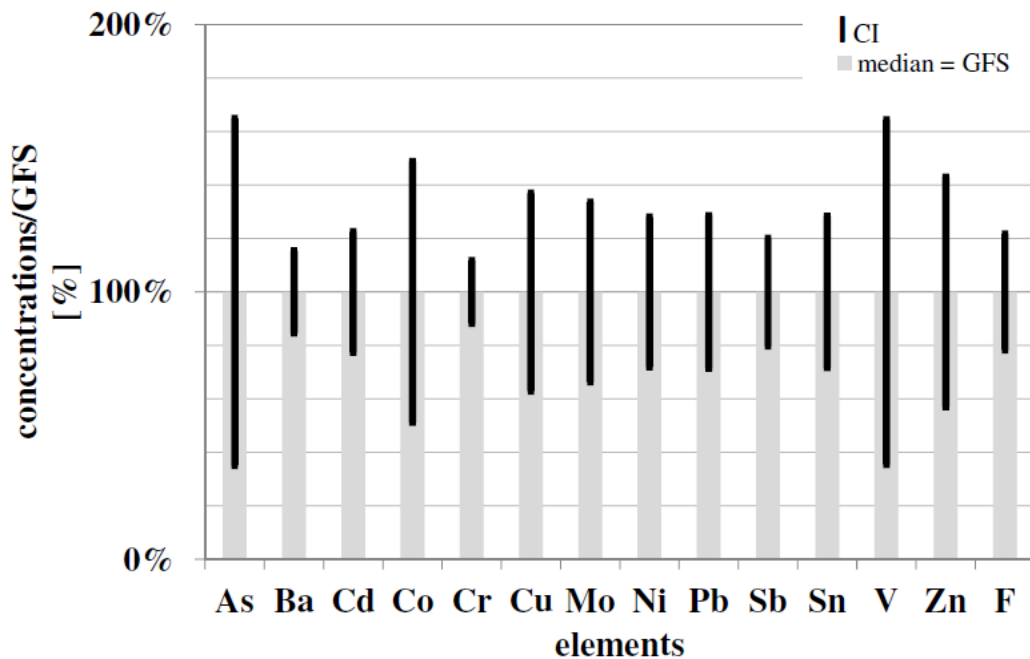


Figure 9: Estimated size of bootstrap percentile confidence intervals ($\alpha = 0.1$) for a field scale median concentrations of trace element in the percolation water that equals the GFS (assumed sample size per site $N = 10$)

What could be evaluated were the effects of the field scale variability on the applicability of the thresholds. One drastic example would be the CI of the field scale median of V concentrations in percolation water. The estimated CI ($\alpha = 0.1$) for the field scale median of concentrations determined from 10 percolation water samples was here $4.6 \mu\text{g/l}$. Assuming a symmetric CI (-2.3 and $+2.3 \mu\text{g/l}$) this would imply that an exceedance of the GFS (V: $4 \mu\text{g/l}$) could only be statistically ($\alpha \leq 0.1$) established if the median was higher than $6.3 \mu\text{g/l}$. On the other hand, to be statistically sure ($\alpha \leq 0.1$) that the medium concentration is below the GFS the median must have been $< 1.7 \mu\text{g/l}$. Generally speaking, due to the spatial variability of soils and the resulting variability in trace element concentrations in the percolation water, statements about exceedance or nonexceedance of GFS values could only be made with acceptable statistical uncertainty ($\alpha \leq 0.1$) when operational median concentrations were about 1/3 higher or lower than their critical GFS.

2.5 Acknowledgements

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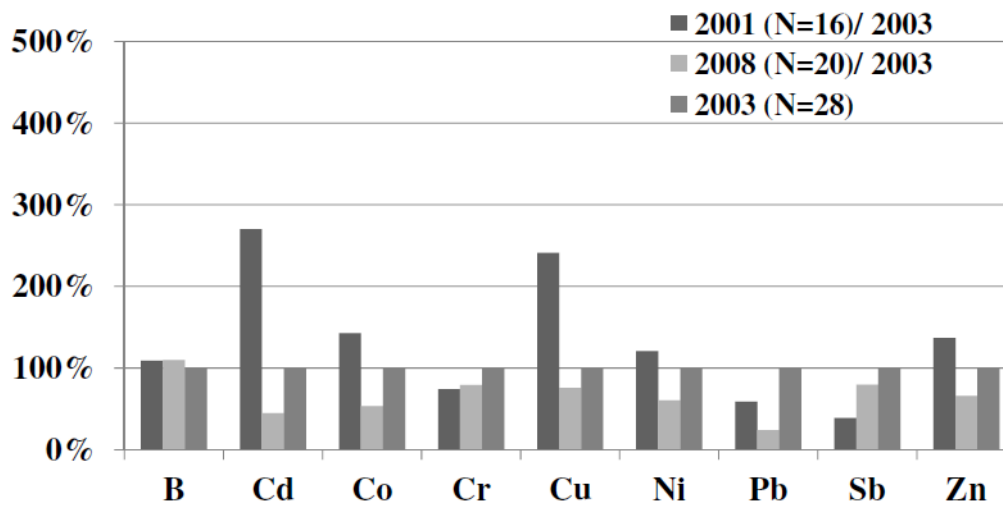
2.7 Supplementary information to the paper

Application of groundwater thresholds on percolation water

-A case study on percolation water from Northern German Lowlands-

2.7.1 Estimation of nonparametric bootstrap percentile confidence intervals

Confidence intervals for the percentiles were approximated via nonparametric bootstrap simulations (Davison and Hinkley 1997). Nonparametric bootstrapping is a computer-intensive resampling method in which a multiple of samples of the original sample size are drawn randomly with replacement from the original sample. The median and the 90th percentile were calculated for each of the 8000 bootstrap realizations resulting in a population of simulated statistics, i.e. medians respectively 90th percentiles. The simplest way of calculating a nonparametric bootstrap percentile confidence interval with one-tailed $\alpha = 0.1$ would be to calculate the 10th percentile from the population of simulated statistics as the lower and the 90th percentile as the upper confidence interval. However, often a bias-correction is necessary, because the mean of the bootstrap population deviates from the corresponding statistic of the original sample. Skewness of the bootstrap population can lead to heavily asymmetric confidence intervals. Thus, in this study confidence intervals are calculated as bias-corrected and accelerated (BCa) nonparametric bootstrap percentile confidence intervals (CI) with one-tailed $\alpha = 0.1$. The BCa method applies correction factors for bias and skewness of the bootstrap population, which are estimated from the normally transformed population of simulated statistics (Davison and Hinkley 1997).



Supplemental Figure S 1: Field scale temporal variability of trace element concentrations in percolation water showing relative medians, the concentrations measured in 2003 equal 100%

Supplemental Table S 1: 90th percentile of aqua-regia-extractable trace element concentrations in the topsoil and in soil from the same sampling depth as the percolation water samples, i.e. transition between unsaturated to water saturated zone in the soil, and precaution values for aqua-regia-extractable contents of trace elements as listed in BBodSchV (1999)

	As	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Sn	V	Zn
	[mg/kg]												
topsoil	6.5	109	0.36	5.93	22.4	14.2	0.42	15.4	29.1	0.44	0.96	35.1	62.1
transition of unstatuated to water saturated zone	9	83	0.13	8.56	19	10.2	0.62	17.1	9	0.29	1.04	30.2	30.2
<i>precaution values</i> <i>soil texture sand</i>	-	-	0.4	-	30	20	-	15	40	-	-	-	60
<i>precaution values</i> <i>soil texture loam/silt</i>	-	-	1	-	60	40	-	50	70	-	-	-	150

Supplemental Table S 2: regression coefficients and coefficients of determination of linear regression models of the relationship between field scale median and field scale inter quartile distance (IQD) of trace element concentrations in percolation water and of the relationship between field scale IQD and $\alpha = 0.1$ bootstrap percentile confidence interval (CI) of the field scale median calculated from 10 samples per site for N = 46 sites

	<i>IQD= int+b*median</i>			<i>CI=int+c*IQD</i>		
	int	b	r ²	int	c	r ²
As	-0.19	1.45***	0.81	0.03	0.89***	0.97
Ba	6.00	0.37***	0.26	1.24	0.83***	0.97
Cd	0.12*	0.49***	0.79	0.01	0.9***	0.95
Co	-0.23	1.15***	0.84	0.19*	0.83***	0.98
Cr	0.18**	0.27***	0.39	0.03*	0.86***	0.97
Cu	-0.29	0.85***	0.91	0.15*	0.86***	0.99
Mo	0.01	0.79***	0.52	0.02	0.85***	0.98
Ni	0.24	0.67***	0.89	0.26**	0.81***	0.99
Pb	0.14	0.68***	0.85	0.06**	0.83***	0.96
Sb	0.02	0.48***	0.62	0	0.84***	0.97
Sn	0.01	0.39**	0.47	-0.01	1.46***	0.84
V	-0.35	1.42***	0.86	-0.05	0.91***	0.99
Zn	2.00	0.95***	0.75	2.31*	0.86***	0.99
F	0.02	0.46**	0.28	0	0.94***	0.98

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

2.7.2 Reference

Davison, A. and D. Hinkley. 1997. Bootstrap methods and their application. Cambridge University Press, Cambridge, New York.

3 Comparing concurrent in situ and batch-extracted trace element concentrations²

Keywords: water soluble trace metal concentration, field-laboratory comparison of trace metal extraction, batch experiments, soil solution, ionic strength adjustment

3.1 Abstract

Different procedures to investigate dissolved trace element concentration at the transition from unsaturated to saturated zone in soils were compared by concurrent sampling of soil solution and solid soil material in this zone. The in situ sampled soil solution from the percolated water was used to measure in situ concentrations, while solid soil material was used to measure concentrations at two liquid/solid ratios using batch experiments on 250 sample pairs. The liquid-solid ratios were 2 l/kg and 5 l/kg. At 5 l/kg the ionic strength was adjusted with $\text{Ca}(\text{NO}_3)_2$ to a sample specific value similar to in situ, while at 2 l/kg the ionic strength was not adjusted. The extracted concentrations of most trace elements exhibited a statistically significant but weak correlation (p -value < 0.01) to the corresponding in situ concentrations. In the liquid-solid ratio of 2 l/kg extracts, Pb and Cr showed very poor comparability with the in situ equivalent. A likely cause was the enhanced DOC release in the extract due to the lower ionic strength compared to in situ conditions in combination with effects from drying and moistening soil samples. For the other elements, correlation increased in the order $\text{As} < \text{Cu}, \text{Zn}, \text{Sb}, \text{Mo}, \text{V} < \text{Cd}, \text{Ni}, \text{Co}$ where adjustment of the ionic strength led to slightly better results. In addition to the element-specific shortcomings, it appeared that low concentration levels of in situ concentrations were generally underestimated by batch extraction methods. The liquid-solid ratio of 2 l/kg extracts could only be used as a method to predict exceedance of thresholds if a safety margin of approximately one order of magnitude

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higher than the thresholds was adopted. The ability of the batch extraction methods to estimate in situ concentrations was equally limited.

3.2 Introduction

Soil protection is a prerequisite for successful groundwater protection because in most cases soils are subject to the input of harmful substances that may subsequently be leached into the groundwater. For this reason, national environmental or soil protection acts, such as the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV), list thresholds specific for the pathway soil-groundwater (BGBl 1999). Exceedance of these thresholds in the transition from the unsaturated to the saturated zone indicates that a suspected harmful quantity of substances is about to reach the groundwater.

Generally there are three main approaches to assessing the load of harmful substances passing through the transition zone:

- direct sampling of soil solution in or above the place of assessment;
- estimation of aqueous extracts of solid soil material taken from the transition zone,
or
- analysis of groundwater concentrations downstream and recalculation of upstream input using a transport model.

Direct sampling of soil solution, for example by means of suction cups in the transition zone, is the ideal approach when evaluating a given situation. However in view of the financial and temporal restrictions on investigations in practice, soil solution sampling is usually not an option. By contrast, sampling of solid soil material is much easier and less costly; as a consequence, measuring trace element concentrations in extracts of solid soil material is currently the preferred method when estimating loads.

The goal was of course to achieve the best possible comparability of results obtained by extracting the trace element concentrations in the in situ soil solution. In order to extract the trace elements from the soil, soil has to be taken from the sampling site, dried and sieved, then moistened with the eluant and shaken. This can alter the soil properties which govern the mobility of trace elements (Jones and Edwards 1993 and Förstner 1992). Sieving, withdrawing and shaking are most likely to influence the physical structure, e.g. by breaking up aggregates and thus creating new surfaces or smaller colloids. Drying can also alter the physical structure depending on clay content, but this most likely affects the chemical properties such as the redox-state and the pH-value. Moistening with an artificial eluant and changing the liquid-solid ratio will also modify the fluid by affecting the ionic strength, the

composition of complexing agents or the solubility of organic carbon. The above are just a few possible effects of sample treatment.

Among others, the pH-value, the redox-state, the physical structure of organic and inorganic solid compounds, the particle size distribution as well as the composition of complexing agents and the ionic strength in a solution are factors governing the solubility of trace elements (e.g. Jordan et al. 1997, Temminghoff 1998 or Voegelin et al. 2003). Each soil and each trace element displays a different sensitivity toward changes in soil properties with regard to the solubility of trace elements. This makes it no longer possible to compare those results obtained by extraction and those gained from in situ soil solution on an ideal, i.e. one-to-one basis.

There are numerous studies comparing trace element concentrations obtained by different extraction methods (Delay et al. 2007, Kalbe et al. 2007, Grathwohl and Susset 2009, Sahuquillo 2003 and Voegelin et al. 2003). Some of these compare different liquid-solid ratios (Fällman and Aurell 1996, Iden and Durner 2008) or compare extracts with soil solution from a lysimeter (Delay et al. 2007, Fällman and Aurell 1996). Mostly such comparisons have been conducted with small sample sizes from a limited number of sites and with medium to highly contaminated material (Sahuquillo et al. 2003, Kalbe et al. 2007 or Rennert et al. 2009). But so far there has been no attempt to compare concentrations from in situ sampled soil solution with results from batch extractions on a large scale using samples taken from many different sites and adopting a homogeneous sampling and analytical approach.

The regulations of the BBodSchV identify the transition zone between the unsaturated and saturated zone to be the place for assessing critical loads for the pathway soil groundwater. Against this background this study aims to test the ability of two different extraction methods to estimate in situ trace element concentration in soil solution. The methods were tested on a set of 250 liquid-solid sample pairs. This set was gained by taking samples at the transition zone from 37 sites in Northern Germany (Duijnsveld et al. 2008). We applied two extraction methods to the solid sample material: firstly, an aqueous batch extract with liquid-solid ratio of 2 l/kg (DIN 19529 2009). This method is designated to be a new standard method (Susset and Leuchs 2008) and is convincing in practice because of its simplicity. The other method is an aqueous batch extract at a liquid solution ratio of 5 l/kg with an ionic strength adjusted to in situ conditions using $\text{Ca}(\text{NO}_3)_2$ (Heidkamp 2005, Utermann et al. 2005). Adjusting the ionic strength is employed to reduce potential differences between the

solution characteristics in the extract and in situ and hence to reduce deviations between the extracted quantities of trace elements. The same approach was applied by Utermann et al. (2005) and Heidkamp (2005) to measure the soluble trace element fraction in sorption experiments that were carried out to derive pedotransfer functions.

Bearing in mind the natural heterogeneity of the soil and the differences in experimental conditions, the following questions arise. To what extent are concentrations of trace elements in batch extracts comparable to in situ concentrations? Does adjusting one soil/solution parameter to in situ conditions contribute to better estimation accuracy? Can the liquid-solid ratio of 2 l/kg (Susset and Leuchs 2008) batch elution method be used to determine whether thresholds or trigger values are exceeded?

3.3 Materials and Methods

3.3.1 Sampling

The 37 sampling sites in Northern Germany were selected by Duijnsveld et al. (2008). In their study, the authors investigated regionally representative background concentrations of trace elements in soil solution from the transition between the unsaturated and saturated zone. The sites were chosen to include the three major parent material classes found in Northern Germany: sand, boulder clay and loess used as arable land. Sandy sites further included two other types of land use: grassland and forest.

The samples, both liquid and solid material, were taken at the transition between the unsaturated and saturated zone at exactly the same depth and location. The total data set consists of 250 sample pairs. Soil solution was gathered with low sorption suction cups having an internal sample collection system (Duijnsveld et al. 2008). The suction cup was made of a nylon membrane and a high density PE body while all parts of the inner sample collecting device were made of PTFE. For sampling of the soil material in the transition zone, a Plexiglas tube was driven into the sediment and a packer system just above the soil sample was used to retrieve the sample (Duijnsveld et al. 2008).

3.3.2 Analytics

Trace element concentrations were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry (ICP-OES). The pH ($\text{pH}_{\text{in situ}}$) and electrical conductivity ($\text{EC}_{\text{in situ}}$) were analyzed on site for the soil solution (liquid samples). The pH-values of the soil sample were measured both in H_2O and CaCl_2 .

All liquid samples were stabilized with 1% HNO₃ and stored under refrigeration in PTFE bottles until analysis in either ICP-MS (Agilent 7500 with a Micro Mist nebulizer) or ICP-OES (Spectro Cirrus Vision with a Crossflow nebulizer). The aliquots for analyzing concentrations of dissolved organic carbon (DOC) were stored in a cool state in 30 ml glass bottles. DOC was analyzed according to DIN EN 1484 (1997) in an Elementar highTOC II analyzer. Due to the limited amount of sample material available, DOC of the extracts was analyzed on a representative sub-sample of 70 samples. Representativeness of the sub-sample was evaluated by comparing the main descriptive location parameters of both samples.

Extraction with adjusted ionic strength

To compensate for the wider liquid-solid ratio of 5 l/kg, Ca(NO₃)₂ was used as a background electrolyte to adjust the ionic strength to natural conditions. The experimental protocol followed here is similar to that in Heidkamp (2005). EC_{insitu} is known from the sampled soil solution. Given that 1 mmol/l of Ca(NO₃)₂ is equal to an ionic strength of 3 mmol/l (1 mmol of Ca and 2 mmol of NO₃), the concentration $c(\text{Ca}(\text{NO}_3)_2)$ of Ca(NO₃)₂ which will be added to the extractant in order to adjust the ionic strength to in situ conditions is calculated as follows:

$$c(\text{Ca}(\text{NO}_3)_2) = \frac{0.013}{3} \left[\frac{\text{mmol}}{\text{L}} \cdot \frac{\text{cm}}{\mu\text{S}} \right] \cdot (\text{EC}_{\text{insitu}} - \text{EC}_{51}) \quad (2)$$

EC₅₁ is the EC in the 5 l/kg extract. To simplify the experimental protocol, the Ca(NO₃)₂ concentrations were classified by rounding to 0.5 mmol/l increments, starting at 0.25 mmol/l. The calculated maximum ionic strength was 17.25 mmol/l.

For extraction, we mixed 7 g of soil with 35 ml of solution in 50 ml PE tubes. To prove the homogeneity of these small samples, 5 repetitions on 7 typical solid samples have been conducted for both extraction methods. The coefficients of variation are displayed in Table 6 and show, that homogeneity of the aliquot soil sample is ensured. The tubes were shaken for 48 h in an end-over-end shaker at 20 rpm. After centrifugation at 3000 g (18°C, 30 min) the extract was decanted and then filtrated through 0.45 µm-pore cellulose-acetate filters. 5 ml of the filtrate was prepared for trace element measurement by diluting and stabilizing the sample with 5 ml of 1% HNO₃. The remainder of the unfiltered supernatant was used to determine electrical conductivity (EC₅₁) and pH (pH₅₁).

Extraction with water at liquid-solid ratio of 2 l/kg

One disadvantage of the method described above was the laborious task of adjusting ionic strength. A much easier alternative is aqueous extraction at a liquid-solid ratio of 2 l/kg. In this alternative, the liquid-solid is closer to in situ conditions and aims to compensate for non-adjustment of ionic strength (Iden and Durner 2008 and Kalbe 2007).

Extraction with ultrapure water was conducted following DIN 19529. 15 g of dry sediment was weighed into a 50 ml centrifuge tube made of polypropylene (PP) and 30 ml of ultrapure water added. The mixture was shaken in an end-over-end shaker for 24 hours at 4-5 revolutions per minute (rpm). The sample was then centrifuged (3000 g, 18°C, 30 min), decanted and filtered through 0.45 µm filters. 10 ml of the filtrate was prepared for trace element measurement by stabilizing with 0.1 ml of 65% HNO₃. The pH-value and the electrical conductivity (pH₂₁ and EC₂₁) were measured in the remaining supernatant.

3.3.3 Statistics

All statistical calculations were conducted using the software packages R (R Development Core Team 2009) and IBM SPSS 18 (SPSS Inc. 2009). Only data pairs displaying accurate adjustment of the ionic strength were used for calculation, so that the difference between EC in the 5 l/kg and in situ was not greater than one class interval of 120 µS/cm. If the EC was smaller than 120 µS/cm the difference between adapted and in situ EC had to be smaller than 20% of the in situ EC. 46 sample pairs did not meet these criteria and were thus eliminated.

The centre of the data cloud comparing the trace element concentrations found in situ and extracted lay in the lower levels of concentration. Additionally, variance analysis revealed heteroscedasticity for all elements. Homogeneity of variances is a crucial presumption for regression analysis. To overcome this problem and to achieve more detailed insight into relations at low concentration levels, further statistical analyses were conducted with log₁₀-transformed data.

Working with log₁₀-transformed data can cause numerous obstacles - especially when the results are retransformed to the Cartesian coordinate system. These problems mostly arise from the fact that the formerly symmetric relationship between upper and lower standard deviation and the mean becomes asymmetric when retransformed. On account of this problem, we preferred non-parametric exploratory and descriptive statistics wherever possible,

such as the median instead of the mean and box-plot analysis to detect outliers and extremes instead of Grubbs test for outliers.

Extremes were removed from the data set as data pairs and were defined as such:

$$x_{Ti} \geq P_{75} + 3 \cdot IQD \quad (3)$$

or

$$x_{Ti} \leq P_{25} - 3 \cdot IQD \quad (4)$$

where

$$IQD = P_{75} - P_{25} \quad (5)$$

P_{25} and P_{75} stand for the first and third quartile of a distribution (SPSS Inc. 2009). 8% of the data pairs had to be removed from the data set.

Data with trace element concentrations smaller than the limit of quantification were also eliminated from the dataset. These elimination criteria affected 8% of the data pairs, i.e. 236 data pairs out of 2926 data pairs. The trace element concentrations were analyzed at discontinuous intervals over a longer period of time. Because of changes in methods and technique over time, different limits of quantification needed to be applied for each period of measurement (Table 6).

Table 6: Data of quality assurance: range of limits of quantification and mean coefficient of variation (COV, calculated from 5 repetitions of 7 samples).

	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	V	Zn
limits of quanti- fication [µg/l]	0.1- 3	0.004- 0.05	0.01- 0.07	0.08- 0.9	0.3- 0.5	0.003- 0.1	0.03- 0.1	0.015- 0.5	0.001- 0.01	0.01- 0.06	0.02- 7
COV LS 2 l/kg [%]	16	6	10	17	11	21	11	13	6	18	9
COV LS 5 l/kg [%]	14	13	12	28	12	18	13	19	9	22	22

LS is liquid solid ratio

To evaluate the relationship and comparability of trace element concentrations in soil solution and in the aqueous extracts, we conducted regression analyses. Since we wanted to evaluate how far extraction methods are valuable tools to estimate in situ concentrations, regression analysis was applied to the trace element concentrations in situ. Hence, in our case y stands for in situ concentrations and x for concentrations in the extracts. Again, this was performed with \log_{10} -transformed data.

$$\hat{y}_T = a_T + b \cdot x_T \quad (6)$$

Confidence intervals for the regression line were calculated for a probability of $p = 0.8$. The confidence intervals were calculated based on the α percentile of t-distribution with the software package R (Sachs and Hedderich 2006).

The confidence intervals in a regression can be used to identify values at which it is possible to detect from concentrations in extracts with a defined probability p that a given concentration y_L , for example a threshold, is exceeded in situ or not. Geometrically, these values consist of the x -value of intersections on a horizontal linear slope at $y = y_L$ and the confidence intervals. Within these borderlines, it is not possible to determine with the aspired degree of certainty whether a set concentration is exceeded or not.

3.4 Results and Discussion

With the exception of Zn the median of the trace element concentrations in the extracts and in the soil solution samples were of the same order of magnitude (Table 7) if compared with each other. Median concentrations of Zn were one order of magnitude lower in the liquid-solid ratio of 2 l/kg extracts than in the in situ soil solution. The listed concentration levels of in situ soil solution may be considered as typical background concentrations for rural, uncontaminated sites (Duijnsveld et al. 2008). As a reference, we compared the values to the German thresholds of the groundwater, the GFS (LAWA 2004). Table 7 shows the median trace element concentrations, which are lower than the thresholds.

The concentrations of trace elements in the liquid-solid ratio of 2 l/kg extract were often higher than in situ or the liquid-solid ratio of 5 l/kg extract. As, Cr, Mo, Pb and V median concentrations in the liquid-solid ratio of 2 l/kg extracts were up to five times higher than the median concentrations measured in situ, while median concentrations in the extract from the liquid-solid ratio of 5 l/kg corresponded quite closely (Table 7). For Cu, Ni and Zn, the in situ medians exceeded the corresponding medians in the liquid-solid ratio of 2 l/kg extracts and liquid-solid ratio of 5 l/kg extracts. The medians of Cd, Co and Sb concentrations were on a similar level in all three kinds of solutions.

Descriptive statistics such as the median give only limited insight into the comparability of data. For a detailed investigation of the relationship between trace element concentrations in situ and concentrations in the extracts, a regression analysis was performed. Table 7 shows the corresponding coefficients of determination. Most extract concentrations displayed a statistically significant but weak relationship to their in situ concentration, except

for Pb at a liquid-solid ratio of 2 l/kg where no correlation could be observed. The coefficient of determination at liquid-solid ratio of 5 l/kg with $r^2 = 0.34$ was also very low. Even poorer, yet still statistically significant results were obtained for Cr.

For the liquid-solid ratio of 2 l/kg, correlation between concentrations of a metal in the in situ soil solution and laboratory batch extract increased in the following order of sequence: Pb, Cr << As < Ni, Cu, Co, V, Zn, Mo, Sb < Cd. For the liquid-solid ratio of 5 l/kg, this order of sequence changed slightly to: Cr << As, Pb, Sb < Cu, Mo < V, Zn, Cd < Ni, Co. These results corresponded to the order of mobility of trace elements (Brümmer et al. 1986), with the least mobile elements showing the poorest correlation. However, even the highest coefficients of determination revealed that no more than 62% of the in situ concentration variance could be explained by the concentrations measured in the extracts (Table 7). For many elements the r^2 was similar for both extracts. If there was a sincere difference between the coefficients of determination the r^2 were usually higher for concentrations of cationic elements (such as Cd or Zn) measured in the liquid-solid ratio of 5 l/kg extracts.

Table 7: Median of trace element concentrations in situ and in the extracts, insignificance thresholds for groundwater (GFS) provided by the German Working Group on water issues of the Federal States and the Federal Government (LAWA 2004) and adjusted coefficients of determination with p-value < 0.01 for the relationship between trace element concentrations measured in situ and in extracts of liquid-solid ratios (LS) of either 2 l/kg or 5 l/kg.

		As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	V	Zn	
		[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	
N		148	246	250	249	250	242	250	188	250	245	221	
GFS		10	0.5	8	7	14	35	14	7	5	4	58	
Median	in situ	0.48	0.07	0.43	0.53	2.56	0.11	2.6	0.3	0.14	0.36	12	
	LS 2 l/kg	0.91	0.05	0.69	1.4	2.15	0.18	1.7	0.72	0.16	1.77	1.51	
	LS 5 l/kg	0.34	0.05	0.35	0.58	0.9	0.12	1.3	0.07	0.12	0.3	5.7	
in situ~ LS 2 l/kg		r^2 adj ^A	0.31	0.53	0.42	0.02	0.41	0.46	0.40	-	0.47	0.45	0.45
		a_T	-0.23	-0.01	-0.05	-0.3	0.18	-0.55	0.34	-	-0.21	-0.36	0.64
		b	0.48	0.77	0.66	0.14	0.56	0.55	0.55	-	0.70	0.53	0.72
		$S_{y_T-x_T}$	0.33	0.55	0.60	0.34	0.41	0.47	0.47	-	0.33	0.48	0.58
in situ~ LS 5 l/kg		r^2 adj ^A	0.29	0.59	0.62	0.18	0.42	0.47	0.60	0.34	0.35	0.56	0.57
		a_T	0.01	-0.10	0.07	-0.12	0.41	-0.40	0.66	-0.18	-0.15	0.06	0.82
		b	0.58	0.68	0.61	0.37	0.60	0.67	0.58	0.45	0.67	0.67	0.66
		$S_{y_T-x_T}$	0.34	0.51	0.48	0.36	0.40	0.54	0.38	0.45	0.37	0.43	0.51

^A r^2 has no dimension; r^2 adj: coefficient of determination adjusted to the sample size, a_T is the axis intercept calculated with \log_{10} -transformed data, b is the regression coefficient, $S_{y_T-x_T}$ is the standard deviation of the residuals calculated with \log_{10} -transformed data; N is the number of samples

In Figure 10 - Figure 12, concentrations of selected elements measured in situ are plotted against concentrations measured in the extracts. Cd was chosen for being a typical cationic metal whereas V stands for metals that occurred as anionic species. On the example of Pb we attempted to illustrate the influences on metals whose equilibrium is coupled with the solubility of the organic carbon in the soil. In the left-hand plots, in situ concentrations are plotted against concentrations in the liquid solid-ratio of 2 l/kg extracts. In the right-hand plots, these are plotted against concentrations in the liquid-solid ratio of 5 l/kg extracts.

Significantly, the variance between all elements around the population mean was in the order of magnitude of one to two. When compared to the one-to-one-line, it became evident on average that some elements were underestimated by extraction while others were overestimated. Bivalent cations such as Cd or Cu were mostly underestimated by the extracts, while elements (mainly anions) that occurred in a speciated form, such as V (Adriano, 2001), were overestimated in the extracts with a liquid-solid ratio of 2 l/kg.

The systematic change in extractability can partly be explained by a change in pH. Table 8 displays median values of individual differences between H^+ activities in the extract and in the soil solution. The H^+ activity was lower in the 2 l/kg extract than in situ (Table 8). The higher pH was caused by the dilution effect compared to the in situ soil solution. Additional negative charge (Appelo and Postma, 2005) occurred when de-ionized water was used as extracting agent. Naidu et al. (1994) reported that the pH of a soil suspension was increased by 0.4 - 1 units when the ionic strength of the suspension was decreased. Since we adjusted the ionic strength to in situ conditions in the extract with the liquid solution ratio of 5 l/kg, the pH in this extract was similar to the one measured in the in situ soil solution.

Table 8: Medians of individual differences in H^+ activities [Mol/l], EC [μ S/cm] and DOC [mg/l] of the sample pairs.

		$[H^+]_{\text{extract}} / [H^+]_{\text{insitu}}$	$[EC]_{\text{extract}} / [EC]_{\text{insitu}}$	$[DOC]_{\text{extract}} / [DOC]_{\text{insitu}}$
N		250	250	70
LS 2 l/kg	~ in situ	0.35	0.16	5
LS 5 l/kg	~ in situ	0.76	0.96	2.7

N is the number of samples, LS is liquid-solid ratio

The relatively higher pH-values should have reduced the solubility of cationic elements and enhanced that of anionic elements. In our case, this was especially true for anionic elements. This can be seen for example in the plots for V where the liquid-solid ratio of 2 l/kg extracts overestimated concentrations in the in situ solution and the liquid-solid ratio of 5 l/kg ex-

tracts did not. Additionally, the change in reaction milieu affected speciation of the metals. For example, Pb at higher pH-values was mostly present as uncharged carbonate, (hydr)oxide or phosphate species (Badaway et al., 2002). These uncharged species desorbed more easily, encouraging enhanced release of these elements in the liquid-solid ratio of 2 l/kg.

For cationic elements, however, this pH-effect was somewhat overshadowed by other effects such as dilution itself. Grathwohl and Susset (2009) report that in batch extraction a decrease in aqueous concentrations correlated to increasing distribution coefficients (K_d , i.e. the ratio of solid and aqueous concentrations after extraction). In our case this practically lead to low concentrations of elements with high K_d , such as Pb ($K_d \approx < 50 - > 1000$ l/kg) or Cr, and correspondingly to greater variability resulting from concentration values close to the quantification limit. The higher K_d caused a somewhat robust behaviour of such elements towards changes in the activity, so that adjusting the ionic strength did not affect the equilibrium to any visible extent. For elements with lower K_d such as Cd ($K_d \approx < 1 - > 10$ l/kg), dilution changed the equilibrium in the liquid-solid ratio of 2 l/kg in favour of the sorbed amounts (Figure 10). The wider liquid-solid ratio of the 5 l/kg extract should consequently have lead to even smaller concentrations in the extracts. But adaption of the ionic strength to in situ conditions in the liquid-solid ratio of 5 l/kg extract attenuated the dilution effect so that concentrations were still lower than in situ however similar as in the liquid-solid ratio of 2 l/kg extract.

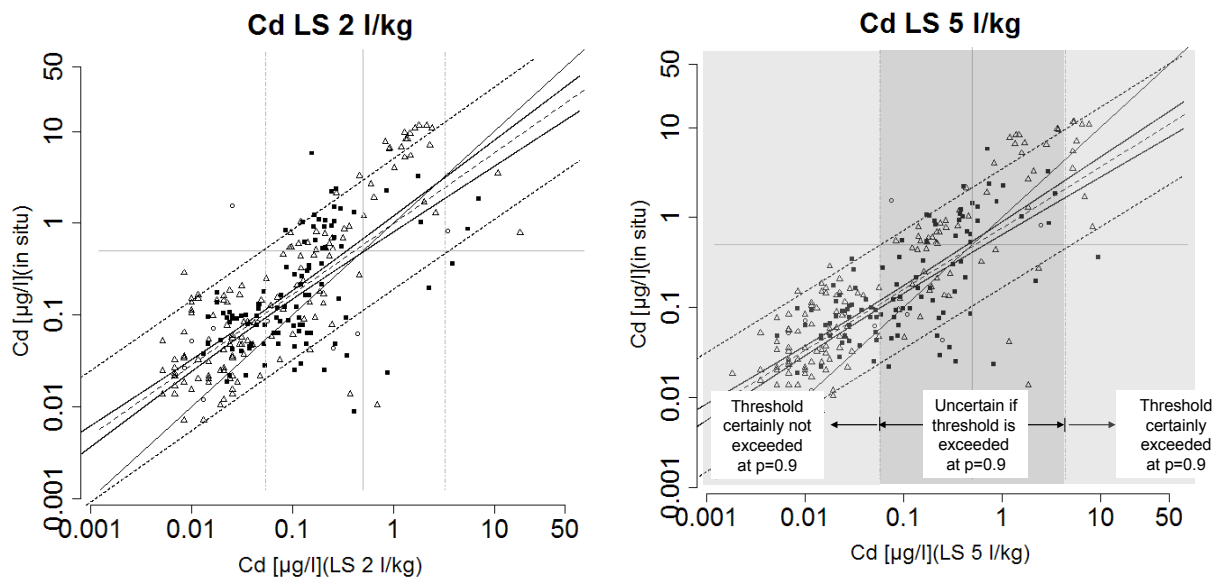
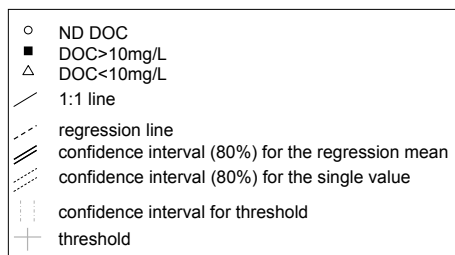


Figure 10: Regression plot of Cd concentrations in liquid-solid ratio (LS) 2 l/kg extract (left) i.e. LS 5 l/kg extract with adjusted ionic strength (right) plotted against Cd concentrations in the in situ soil solution. Unbroken diagonal black line = 1:1 line, broken dark line = regression line, unbroken black curves = confidence interval (80%) of the regression mean, dashed black curves = confidence interval (80%) of the single value, unbroken horizontal and vertical grey lines = threshold, vertical dash-and-dotted grey lines = confidence interval (80%) of the threshold, ■ = soil solution with DOC < 10 mg/l, Δ = soil solution with DOC > 10 mg/l, o = no DOC value available



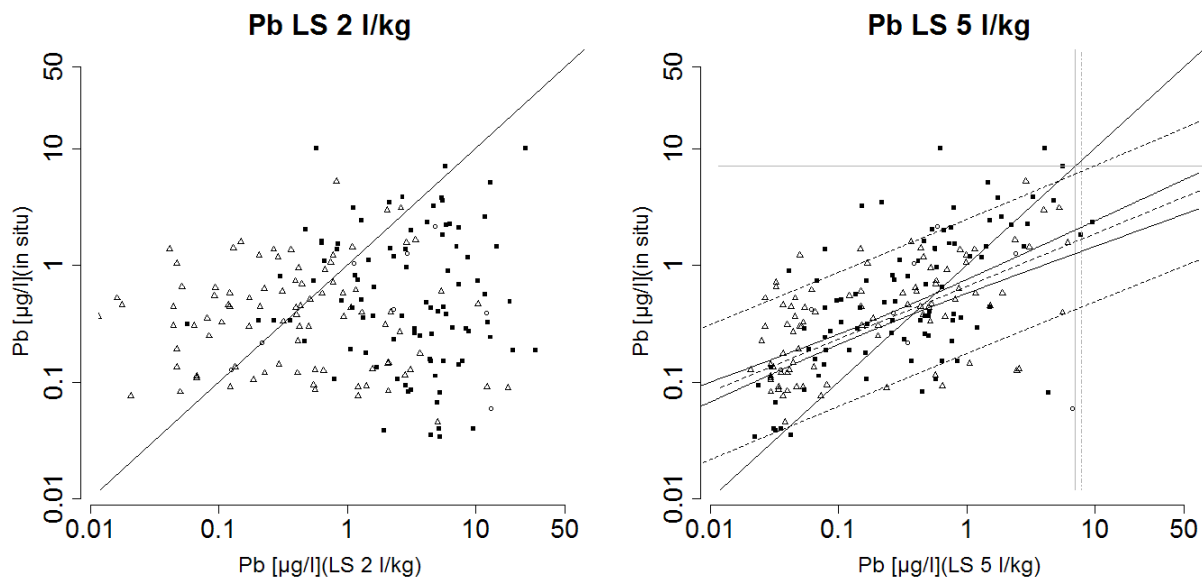
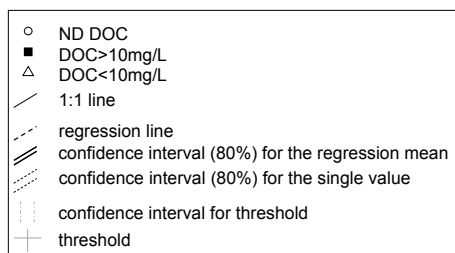


Figure 11: Regression plot of Pb concentrations in liquid-solid ratio (LS) 2 l/kg extract (left) i.e. LS 5 l/kg extract with adjusted ionic strength (right) plotted against Pb concentrations in the in situ soil solution. Unbroken diagonal black line = 1:1 line, broken dark line = regression line, unbroken black curves = confidence interval (80%) of the regression mean, dashed black curves = confidence interval (80%) of the single value, unbroken horizontal and vertical grey lines = threshold, vertical dash-and-dotted grey lines = confidence interval (80%) of the threshold, ■ = soil solution with DOC < 10 mg/l, Δ = soil solution with DOC > 10 mg/l, o = no DOC value available



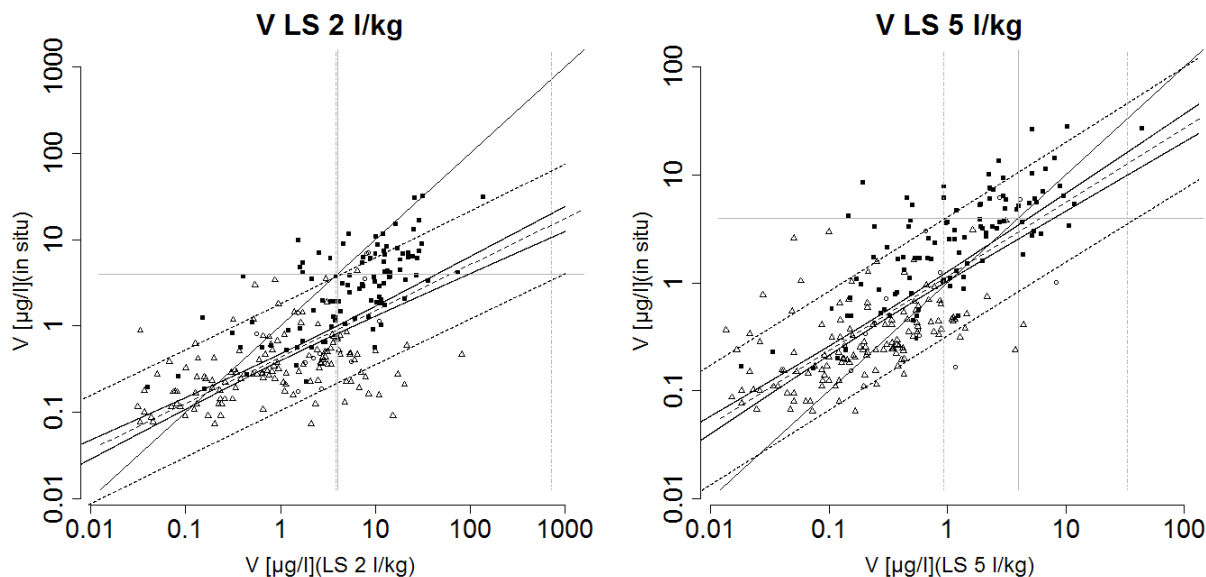
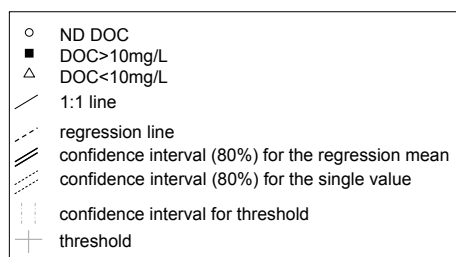


Figure 12: Regression plot of V concentrations in liquid-solid ratio (LS) 2 l/kg extract (left) i.e. LS 5 l/kg extract with adjusted ionic strength (right) plotted against V concentrations in the in situ soil solution. Unbroken diagonal black line = 1:1 line, broken dark line = regression line, unbroken black curves = confidence interval (80%) of the regression mean, dashed black curves = confidence interval (80%) of the single value, unbroken horizontal and vertical grey lines = threshold, vertical dash-and-dotted grey lines = confidence interval (80%) of the threshold, ■ = soil solution with DOC < 10 mg/L, Δ = soil solution with DOC > 10 mg/L, o = no DOC value available



The scatter plots of Pb nevertheless showed that Pb concentrations in situ were not correlated to concentrations in the liquid-solid ratio of 2 l/kg extract (Figure 11). Compared to the one-to-one line, Pb concentrations were overestimated in the liquid-solid ratio of 2 l/kg extract. The enhanced dissolution of Pb in the 2 l/kg extract was probably induced by an enhanced dissolution of Pb-organic carbon complexes into DOC. Analysis on a sub-sample (70 samples) showed that mobilization of organic carbon into DOC was especially increased in the 2 l/kg extract (Table 8).

Part of the enhanced solubility of organic carbon in the extracts was most likely due to re-moistening effects (Jones and Edwards 1993) or to mechanically induced artefacts in the extraction process; this applied for both kinds of extracts. But the exceeding DOC concentrations in the liquid-solid ratio of 2 l/kg were primarily the result of reduced ionic strength in the extract. Temminghoff (1998) reports that $\text{Ca}(\text{NO}_3)_2$ lead to enhanced coagulation of organic molecules, because Ca acted as a bridge between these molecules. Oosterwoud et al. (2009) defined Ca, Mg, Al and Fe to be binding cations, detecting that DOC concentrations in

surface water decreased with increasing cation concentration. The EC characterizes the ion load of a solution. The 2 l/kg extract had a significantly lower EC than the soil solution in situ or the 5 l/kg extract (Table 8).

The results found in the extracts deviated from those in the in situ solution by up to two orders of magnitude. When for example exceedance of the German insignificance threshold for Cd ($x_L = 0.5 \mu\text{g/l}$, LAWA 2004) was assessed by the 2 l/kg extract with a probability of $p = 90\%$ the sincere variability of the data clearly affected the quality of the results obtained by these methods, especially when very small concentrations were evaluated. The principle of this kind of calculation is shown in the right-hand graph in Figure 10. The assumption of Cd concentrations exceeding the threshold in situ could only be made with the aspired probability at Cd concentrations greater than $3.2 \mu\text{g/l}$ in the extracts. Non-exceedance of Cd in situ could be assumed with the designated probability when Cd concentrations in the 2 l/kg extract were lower than $0.05 \mu\text{g/l}$. The area of uncertainty extended over almost two orders of magnitude. In this area, other methods must be adopted to assess exceeding thresholds. For other elements such as V, the systematic difference between concentrations in situ and in the extract was more severe (Figure 12). The difference led the area of uncertainty to shift towards higher concentrations, so that it became increasingly difficult to estimate if a threshold had been exceeded. If the upper confidence line met or passed through the intersection of the one-to-one line at point $y_L = x_L$, it was impossible to detect with the aspired certainty whether the concentration in situ is smaller than the threshold. In this case the values can either be converted (Table 7) or a more accurate method, such as percolation extracts (Grathwohl and Susset 2009) or in situ soil solution sampling (Duijnsveld et al. 2008), should be used. But even if values were converted, the large interval of uncertainty still stands.

3.5 Conclusion

The ability of the batch extraction methods to estimate in situ concentrations was equally limited. All comparisons of trace metal concentrations in the soil solution with those in the extract exhibited a high variance of one to two orders of magnitude compared to the one-to-one line in the concentration levels tested. The results showed that data gained by batch experiments should primarily be used for exploratory purposes during risk assessment. For assessment of Pb and Cr concentrations, the liquid-solid ratio of 2 l/kg was unsuitable. Ad-

justing one sorption parameter improved estimation accuracy, so providing feasibility allows ex situ conditions should be as close as possible to in situ conditions.

In the concentration range of trigger or insignificance values of German legislation, in situ concentrations were underestimated for all elements and for both extraction methods. Transforming concentrations measured in the extracts by means of the given regression coefficients reduced estimation error in terms of under- or overestimation, but did not affect the width of the confidence interval. Reliable prediction of in situ concentrations by applying batch methods was only possible for concentrations that were at least one order of magnitude higher than the legislative insignificance values. As a consequence, at the level of background concentrations referred to in the transition from the unsaturated to the saturated zone these methods are not useful to assess exceedance of trigger values or thresholds.

3.6 Acknowledgements

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4 Nonparametric uncertainty and sensitivity analysis of field scale application of generally applicable empirical sorption isotherms³

Submitted for publication

4.1 Abstract

This study quantitatively analyses different sources of uncertainty that accompany predictions of initial exchangeable solid phase concentrations of Cd, Cr, Cu, Ni, Pb or Zn on a field scale level with straight forward nonparametric statistics. We make a difference between informational sources of uncertainty, namely model error and uncertainty of the measure of central tendency (confidence interval of the median), and uncertainty of the single value due to natural variability. In terms of natural variability we focus on the lateral spatial variability within a horizon. Semi empirical pedotransfer functions (PTF) based on extended Freundlich equations were applied to predict the potentially exchangeable solid phase concentrations (S₀) from common soil properties such as pH, C_{org} and cation exchange capacity, and soluble trace element concentrations. Two sites, typical for northern German lowlands in terms of soil types (gleyic cambisol and haplic luvisol) and texture (sand and silt) were tested. Each soil is in one or more properties at the edge of the validity range of the PTFs in question. Soluble trace element concentrations used to predict S₀ are in a background concentration level. For S₀ predictions in horizons where adsorption was the predominant retention mechanism uncertainty due to spatial variability was larger than or as large as uncertainty due to model error. PTF for Cr prediction was not sufficiently reliable, since model error was by a large amount the main source of uncertainty. Beyond pH 6.5 although within the statistical range of validity, PTF predictions of Ni and Zn were not reliable due to structural changes in the sorption behavior. Calculated from N = 10 - 20 samples the uncertainty of the median was always smaller than the uncertainty of the single value. We conclude that PTF based on

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Freundlich sorption isotherms are a fairly reliable tool to estimate potentially exchangeable solid phase concentrations for soils when sorption is the key retention mechanism and when an uncertainty of ± 0.5 orders of magnitude is acceptable.

4.2 Introduction

In risk assessment for ground water contamination transport models are often applied. The retention of trace elements in the soil in lower concentrations can be described by non-linear Freundlich equation in so called sorption isotherms (e.g. Sposito 1989, Elzinga 1999, Groenenberg et al. 2010, Anagu et al. 2009, Deurer and Böttcher 2006). In order to achieve a broader applicability of the sorption isotherm, general purpose pedotransfer function (PTF) were derived by extending the Freundlich coefficient based on common soil properties governing the sorption behavior (e.g. van der Zee and van Riemdijk 1987, Boekhold and van der Zee 1991, Streck and Richter 1997). The PTFs in the focus of this study are general purpose PTFs for the elements Cd, Cr, Cu, Ni, Pb and Zn valid for soils of arable or grassland. Parameterization of the PTFs was done performing multiple regression analysis of sorption data measured on a nationwide sample of arable and grass land soils (Utermann et al. 2005).

Usually perceived as a quality of nature, diversity or heterogeneity of soil properties leads to uncertainty in estimations and predictions made about of the soil. For a realistic interpretation of the result and informed decision making the uncertainty of input and output parameters need to be considered.

Variation of the model output can result either from informational uncertainty or natural variability (Keller et al. 2002, Frey and Burmaster 1999, Loucks et al. 2005). The processes determining soil formation are physical and chemical and thus obey physicochemical laws. In our example this would imply that the solid phase concentration of a trace element in the soil could be exactly described if all contributing factors were known. But physicochemical properties interact in a way that is highly non-linear, so that the sensitivity of these processes to e.g. small variations in texture combined with local positive feed-back produces chaos. Thus, we are probably not mistaken if we assume that soil properties own some random variability, which cannot be described by physicochemical laws and thus cannot be predicted. The PTF examined in this uncertainty analysis were derived on a broad variety of soil types, and thus take only those contributing factors into account which govern the retention of trace elements in the majority of soils (Utermann et al. 2005). Additionally to the unpredictable random error, it is always possible that on selected soils other physicochemical soil

properties or processes than the selected predominantly affect the retention of trace elements in those soils. The variance caused by the ignorance of other governing factors is subject to informational uncertainty and is reflected in the model error. Another source of informational uncertainty also reflected in the model error is the approximative character of the mathematical equation describing the PTF. The underlying assumption of sorption isotherms based on Freundlich equations is a log-linear relation between concentrations of sorbed and dissolved trace elements (Sposito 1998). Suddenly increasing or decreasing retention of trace elements for example due to co-precipitation or increased mobility of organic carbon respectively cannot be described by a log-linear function and will thus lead to model error. Additionally to the uncertainty cause by spatial variability, the uncertainty of the prediction will thus also be affected by the inaccuracy of the model. In a review of numerous PTF for the estimation of solid phase concentrations of trace elements Elzinga et al. (1999) found low accuracy of PTF, especially for low concentration values (Cd < 0.6 mg/kg, Zn < 9.6 mg/kg and Cu < 18 mg/kg).

Both random and predictable variations in trace element concentrations are a property of nature. Studies did show that trace element concentrations in the soil water are highly variable within small distances (Strebel et al. 1993, Teichert 2001, Heredia and Cirelli 2009 and Godbersen et al. 2012). A large proportion of the uncertainty due to spatial variability can be found within the field scale (10^2 m). Altfelder et al. (2007) found that in average 70% of the variance in prediction uncertainty of estimates for the adsorbed concentrations of Cd was due to field scale variance and only 30% were due to variance of soil properties in between different fields. Garten et al. (2007) discovered that the spatial variability of soil properties, such as C_{org} concentrations, was as variable at small scales (1 - 10 m) as it was at scales of 50 - 500 m. Heidkamp (2005) assumes in his dissertation on the derivation of generally applicable PTFs for forest soils that a great deal of unexplained uncertainty may originate from the field scale spatial variability of the initial amount of trace element in the soil water. He pointed out that if natural variability of the trace element concentration is the predominant source of uncertainty, further attempts to increase the accuracy of estimation for PTF will be ineffectual (Heidkamp 2005).

For purposes of exploratory risk assessment the central tendency (median) of trace element in soils of a designated area are estimated based on a onetime sampling event. The uncertainty of the median is an informational source of uncertainty because it can be reduced by

increasing the sample size. The spatial variability is likely a source of uncertainty, because the spatial variability of the input parameters will propagate through the PTF and directly affect the uncertainty of the median of predictions (Finke et al. 1996, Wösten et al. 2001). The power of the median value decreases with increasing spatial variability.

The important difference between natural variability and informational uncertainty is that informational uncertainty can be reduced to some extent by increased research efforts (e.g. adjusting the model parameters or increasing the sample size). In contrast, uncertainty of the single estimate due to natural variability as a property of nature cannot be reduced. If, for example, the uncertainty due to spatial variability is larger than uncertainty due to informational sources, further efforts on model calibration or sampling will be unrewarding.

Based on the various reports on large variability of soil properties within short distances (e.g. Strebel et al. 1993, Teichert 2001, Altfelder et al. 2007, Garten et al. 2007, Heredia and Cirelli 2009 or Godbersen et al. 2012) our hypothesis is that spatial variability will be the predominant source of uncertainty of PTF predicted trace element concentrations for soils where adsorption is the key retention mechanism for trace elements. We assume, that PTF predictions base on Freundlich isotherms for soils with near neutral and neutral pH, although technically within the range of validity, will not be as accurate because other retention mechanisms become more important and will lead to non-log-linear retention behavior.

The objective of our study is to quantify the different sources of uncertainty that accompany the PTF estimates of the initial exchangeable solid phase concentrations of Cd, Cr, Cu, Ni, Pb or Zn on a field scale level with straight forward nonparametric statistics. We make a difference between informational sources of uncertainty, model error and uncertainty of the median, and uncertainty due to natural variability, reflected in the uncertainty of the single value. In terms of natural variability we focus exclusively on the spatial variability. The estimation of potentially exchangeable solid phase concentrations S_0 will be conducted by applying PTF developed for the application on arable land. We chose two example sites with different soil types and texture each in one or more properties at the edge of the validity range of the PTFs in question. The selected soils are typical for the Northern German Lowlands. Both soils contain soluble trace element concentrations in a background level. The results of the uncertainty analysis can support developers and users of pedotransfer functions in their decision as to whether to invest further resources in an increased number of samples, optimization of pedotransfer functions or a combination of both.

4.3 Materials and methods

4.3.1 Pedotransfer functions PTF

The PTF applied in this study are based on the Freundlich equation in which S represents the solid phase concentration [$\mu\text{g}/\text{kg}$], K_f the Freundlich coefficient, C the soluble concentration of the trace element [$\mu\text{g}/\text{l}$] and m the Freundlich exponent.

$$S = K_f \times C^m \quad (7)$$

Linearization is possible by logarithmic transformation. Extending the Freundlich coefficient by sorption relevant soil properties V_i leads to a more general applicability.

$$\log_{10} S = \log_{10} K_{f-in} + \sum_{i=1}^n \beta_i \log_{10} V_i + m \times \log_{10} C \quad (8)$$

K_{f-in} is the intrinsic Freundlich coefficient. Utermann et al. (2005) offer several combinations of input variables V_i for every element PTF, including soil clay, CEC , aqua regia extractable Fe and Al, soil organic carbon C_{org} and oxalate extractable Fe, Al and Mn. In the PTF with the highest accuracy, i.e. the highest coefficient of determination r^2 , the Freundlich coefficient is extended by the variables H^+ [mol/l], CEC [mmol_c/kg], Mn_{ox} [mg/kg] and C_{org} [$\text{mass } \%$] (Table 9).

Table 9: Coefficients of the PTFs with the highest accuracy on the training data set by Utermann et al. (2005)

	K_{f-in}	$\beta \text{ pH}$	βC_{org}	βCEC	βMn_{ox}	$n C$	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

The PTF have been derived on a large variety of samples and for a wide range of solid phase concentration (Utermann et al. 2005). Models are generally only valid for the condition in which they have been developed. Hence the endpoints of the datasets on which the PTF was parameterized, mark the range of validity for future applications of the PTF. Where applicable, the endpoints of the range of validity (Table 10) are marked in the figures presenting the input data (Figure 15 - Figure 18).

Table 10: Range of validity for the PTF by Utermann et al. (2005) (assembled from original training dataset of the PTF)

	pH _{CaCl2}	CEC [mmol _c /kg]	C _{org} [mass-%]	Mn _{ox} [mg/kg]	C [µg/l]
Cd	3.5-7.6	1.29-427	0.02-11	0.93-3090	0.01-3177
Cr	3.5-7.6	1.29-589	0.03-11	1.62-3090	0.2-1636
Cu	3.5-7.6	2.29-380	0.02-9	0.93-2399	0.4-9380
Ni	3.5-7.6	1.29-589	0.02-11	0.93-3090	0.14-6874
Pb	3.6-7.6	1.29-380	0.02-11	0.93-3090	0.27-42204
Zn	3.6-7.5	1.29-427	0.03-11	0.93-3090	1.61-872874

4.3.2 Sites and samples

The selected soils are typical for the Northern German Lowlands. Both soils contain soluble trace element concentrations in a background level. The first soil is a sandy gleyic cambisol located northeast of Hannover near the village of Hohenzethen in the east of Lower Saxony, Germany. The A-horizon is followed by the cambic horizon (Bv), which smoothly transitions (Bv-Cv) into a weathered C-horizon (Cv) above a gleyic horizon Go(Cv) (Figure 15, also showing soil properties). The gleyic horizon showed thin dark and light red (hydr-)oxide layers marking recent ground water tables. At the day of sampling the ground water table lay at ca. 150 cm below surface. Geologically the soil is located in the quaternary moraine landscape formed during the Drenthe stadium of the Saale glacial period (LBEG 2011). Parent material is glacial sand with small amounts of gravel and < 20% of clay and silt over glaci-fluvial sand over deep basin silt. In this cambisol the pH values range from 4.3 to 7.2. The C_{org} concentrations (0.02 to 1.19 mass-%) show a similar pattern as in the luvisol as they gradually decrease with increasing depth. Most samples of the subsoil showed Mn_{ox} concentrations below the limit of quantification.

The second soil is positioned south of Hannover at the northern edge of the Lower Saxonian loess belt near the village Ohlendorf. Nine horizons were classified in this haplic luvisol (Figure 17). The topsoil of the Haplic Luvisol developed a clear plowing line at about 30 cm below surface (Alp) and shows albic properties down to about 50 cm (Al), directly followed by an argic horizon (Bt) above a deep cambic horizon (Bv). The argic horizon (eICv) has small diffuse hydromorphic signs, such as small spots with ferroxid and manganese concretions alternating with bleaching sings. The prefix "II" marks a change in parent material from loess to sand (Figure 17). The C horizons below the change of parent material from loess to sand (IICv1, IICv 2 and IICv3) shows pronounced hydromorphic signs of dark red rust coatings of

the sand grains. The soil has developed on alluvial periglacial aeolic deposits over glacialfluvial deposits of the Saale glacial period (LBEG 2011). The loess layer reaches from the top down to 100 - 130 cm below surface followed by a sandy layer. The ground water table was at 260 cm to 320 cm below surface. The haplic luvisol shows neutral to alkali pH values (6.1 to 8.0) and CEC from 20 - 120 mmol_c/kg. The C_{org} concentration in the haplic luvisol gradually decreases with increasing depth from a median 1.24 mass-% in the topsoil to 0.01 mass-% in the subsoil. Samples with C_{org} < 0.02 mass-% or pH > 7.6 are out of the range of validity and are excluded from the database. Mn_{ox} concentrations range from 36 - 1425 mg/kg in the luvisol and in the cambisol from < 0.5 to 120 mg/kg.

4.3.3 Experimental

On both sites samples were taken from every horizon on 20 points each from the topsoil to the transition of the unsaturated to the saturated zone. Samples were taken from the cores of percussion coring tubes. The sampling points were aligned in two transects of 10 samples with a distance of 10 m in between two points. All samples were transported in bags made of fluorinated ethylene propylene (FEP) into the laboratory, sieved < 2 mm, dried at 40°C and stored dry in polystyrene containers with polyethylene terephthalate lids.

Utermann et al. (2005) derived most of the PTF by using the interchangeable trace-element fraction determined by isotope dilution mass spectrometry (Gäbler et al. 2007), which is the preferable method to determine the fraction of trace elements that is able to interact with the soluble phase in a short time period. However, since this method is not widely available in this study the solid phase concentration was represented by the Na₂-EDTA extractable concentration of trace elements (Heidkamp 2005 and Godbersen et al. 2012) which extracts a very similar fraction of solid phase concentrations (Utermann et al. 2005). S₀ was calculated as the measured Na₂-EDTA-extractable concentration minus the soluble trace element concentration (C₀). The soluble concentration was estimated by 5 l/kg aqueous batch extraction in which the ionic strength of the extracting agent was adjusted to in situ conditions with Ca(NO₃)₂ as background electrolyte (Heidkamp 2005 and Godbersen et al. 2011). The extracts were mixed at 20 rpm for 48 h subsequently centrifuged for 30 min with 3000 g at 18°C. The extract was then decanted and filtrated through 0.45 µm pore cellulose-acetate filters. The pH value was measured potentiometrically in a 0.01 mol/l CaCl₂ suspension (ISO 10390:1994). The difference between total carbon measured in elemental analysis (vario MAX, elemental) and carbonate carbon (Scheibler's apparatus) represents the concentration

of organic carbon (C_{org}). The effective cation exchange capacity (CEC) was measured in 0.1 mol/l $BaCl_2$ percolates. The particle size distribution was determined on a maximum of $N = 4$ samples out of $N = 20$ per horizon by the pipette method developed by Köhn (DIN ISO 11277:2002-08). Trace element concentrations were analyzed with a magnetic sector inductively coupled plasma-mass spectrometer (ICP-MS, agilent). Cationic elements have been measured with inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro). Limits of quantification were calculated from the nine fold of the standard deviation of the blind values (Table 11). Data smaller than the limit of quantification were excluded from uncertainty and sensitivity analysis.

Table 11: Limits of quantification

	Cd	Cr	Cu	Ni	Pb	Zn
C [$\mu\text{g/l}$]	0.004	0.05	0.06	0.05	0.02	0.1
S [$\mu\text{g/kg}$]	0.8	15	50	20	20	100

4.3.4 Uncertainty analysis

Uncertainty can come from informational uncertainty and from the natural heterogeneity of the soil (Keller et al. 2002 and Frey and Burmaster 1999). Informational uncertainty can result from to e.g. incomplete samples, measurement errors or incorrect model assumptions, which can all be reduced to a certain amount by increased efforts. Natural heterogeneity is caused by spatial and temporal variability. In this project the data stem from a onetime sampling event and we only consider the spatial variability.

The uncertainty of predictions depends on the accuracy and precision of the prediction (Bolker 2008). The accuracy characterizes correctness of the prediction. The precision indicates the detail resolution of an estimate. The inter quartile distance (IQD) is chosen as a measure for spatial variability and quantifies the uncertainty or representativeness of a single value for a given area (Figure 13). The median represents the central tendency of the data. The uncertainty of the median, quantified by nonparametric $\alpha = 0.1$ bootstrap percentile confidence interval (CI), characterizes the precision of the median. The methodology to derive bootstrap confidence intervals is described in Davison and Hinkley (1997). CI is a measure of informational uncertainty because it can be reduced by increasing the sample size. The difference between the predicted (S_{PTF}) and the measured adsorbed trace element concentration (S_{EDTA}) represents the model error. The prediction uncertainty for one horizon is quantified by the median of absolute model error (MAE).

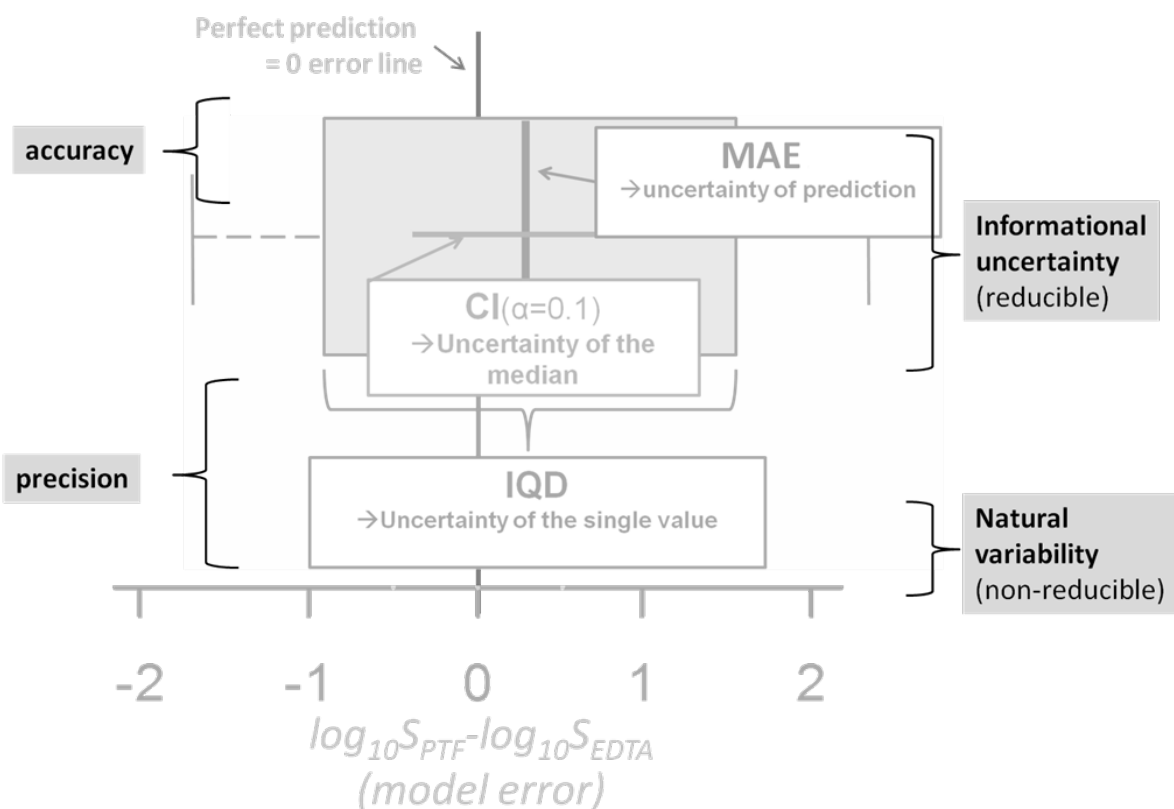


Figure 13: Measures of uncertainty in sorbed trace element concentrations predicted with general purpose pedotransfer functions (PTF). MAE median of absolute model error (absolute difference between PTF predicted concentration S_{PTF} and concentration of trace elements in Na_2 -EDTA extracts S_{EDTA}) represents the uncertainty of prediction and is a measure of accuracy and informational uncertainty; CI nonparametric bootstrap percentile confidence interval of the median, represents the uncertainty of the measure of central tendency and is a measure of precision and informational uncertainty; IQD inter quartile distance, represents the uncertainty of the single value and is a measure of precision and natural variability

Nonparametric estimators were used to characterize the data, because normal distribution of our data cannot be assumed. Uncertainty assessment was done horizon-wise. In soils trace element concentrations often show a large vertical variability. To be able to compare the uncertainty from one horizon to the other, the measures of uncertainty were calculated with \log_{10} -transformed data. The chosen measures of uncertainty are all differences of some sort (Figure 14). The CI is the difference between the 90th and 10th percentile of the \log_{10} -transformed population of bootstrap replicates of the median. The difference between the 3rd and 1st quartile of the sample population is the IQD and the model error is the difference of predicted and measured \log_{10} -transformed solid phase concentrations of trace elements. Differences of \log_{10} -transformed data translate into dimensionless quotients in Euclidean space and are comparable independent of the underlying concentration level.

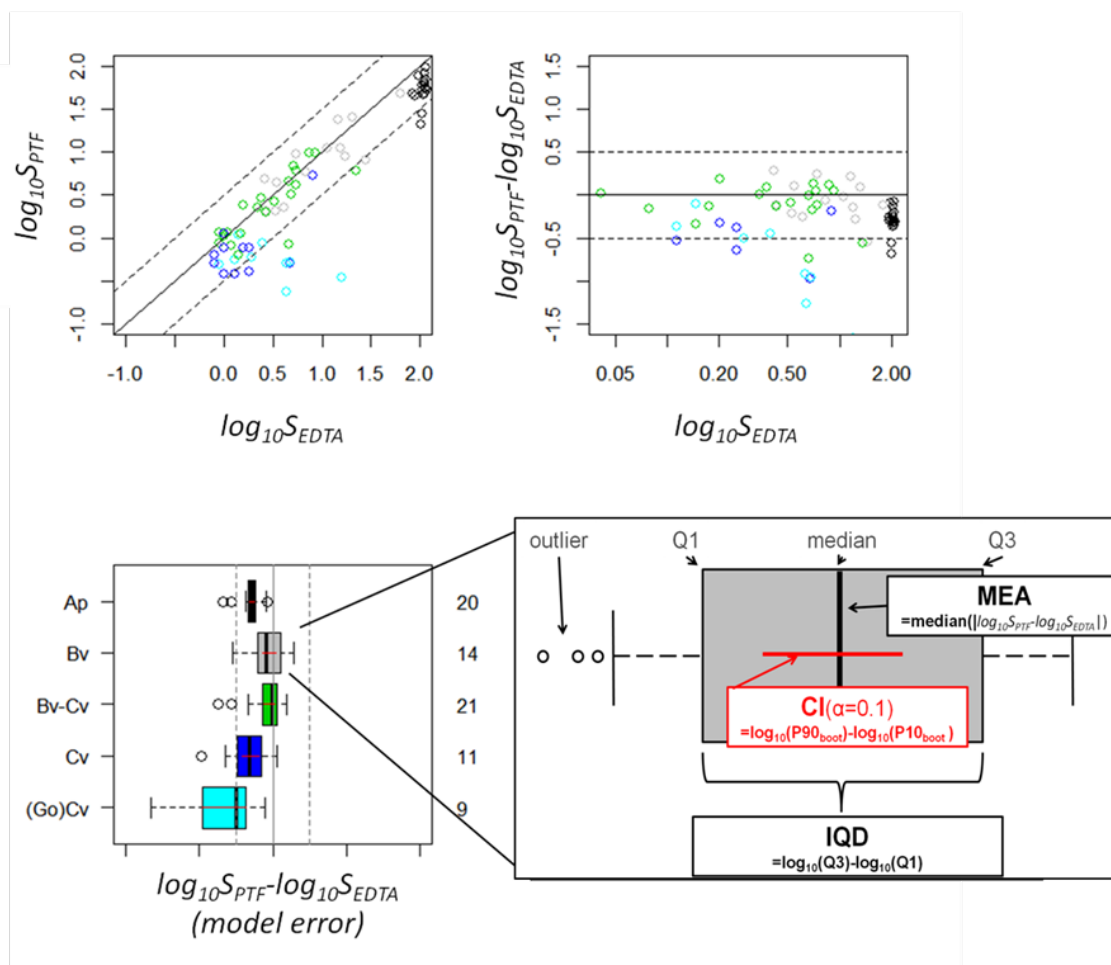


Figure 14: Construction of median absolute model error (MEA), confidence interval of the median (CI) and inter quartile distance (IQD). Top left: scatter plot of PTF predicted concentration S_{PTF} and concentration of trace elements in Na_2 -EDTA extracts S_{EDTA} . Top right: comparing model error ($\log_{10}S_{PTF}-\log_{10}S_{EDTA}$) and S_{EDTA} ; bottom left: horizon wise box plots of model error; bottom right: legend of box plot, Q1 1st quartile, Q3 3rd quartile, $P90_{boot}$ 90th percentile of the population of bootstrap replicates of median, $P10_{boot}$ 10th percentile of the population of bootstrap replicates of median

Based on an approach taken by Blukacz et al. (2005) the uncertainty analysis was conducted by bootstrapping the prediction of the PTF. The bootstrap uncertainty analysis consisted of the three steps: randomization, transformation and aggregation. Randomization means the bootstrap resampling of the vector of input parameters $v_i = (c(H^+)_i, CEC_i, C_{org\ i}, Mn_{ox\ i}, C_i)$ from the existing database. Efron and Tibshirani (1993) suggest $N_b = 1000$ or more iteration for the simulation of confidence intervals. We used $N_b = 8000$ iterations because then simulation error was $< 1\%$. In the transformation step the PTF was applied and in the aggregation step the median, inter quartile distance and the nonparametric bootstrap percentile confidence intervals were calculated.

Throughout the study we use the terms very small (< 0.1 orders of magnitude), small (0.1 - 0.35 orders of magnitude), moderate (0.35 - 0.65 orders of magnitude), large (0.65 –

1 orders of magnitude) and very large (> 1 order of magnitude) to describe the widths of IQDs or CIs.

4.4 Results and discussion

4.4.1 Input data

The soluble trace element concentrations decreased with increasing depth (Figure 16 and Figure 18). Soluble Cr concentrations increased in the Bv and eCv and especially in sandy layer of the luvisol. This may be due to a change of the speciation around pH 7 from CrOH^{2+} into CrO_4^{2-} (Takeno 2005). Both soils showed a similar range of soluble Cd concentrations (< 0.004 - 0.2 $\mu\text{g/l}$). For Cr and Ni the luvisol showed a wider range (Cr: < 0.05 - 3.9 $\mu\text{g/l}$, Ni: < 0.05 - 3.1 $\mu\text{g/l}$) than the cambisol (Cu: 0.08 - 1.1 $\mu\text{g/l}$, Ni: 0.3 - 2.3 $\mu\text{g/l}$). Soluble Cu, Pb and Zn concentrations were lower in the luvisol (0.06 - 7.5 $\mu\text{g/l}$) than in the cambisol (0.3 – 14 $\mu\text{g/l}$).

The physicochemical soil properties of the gleyic cambisol needed as input variables in the PTFs are shown in Figure 15. In the majority of horizons the soil properties were within the range of validity (Table 10). The silt and clay content of the deepest horizons was lower than the minimum of the training data set. However, since the particle size was not considered in the PTF it should not affect the applicability. Soluble trace element concentrations C0 were at the edge of the range of validity or even smaller than the lower boundary of validity (Figure 16).

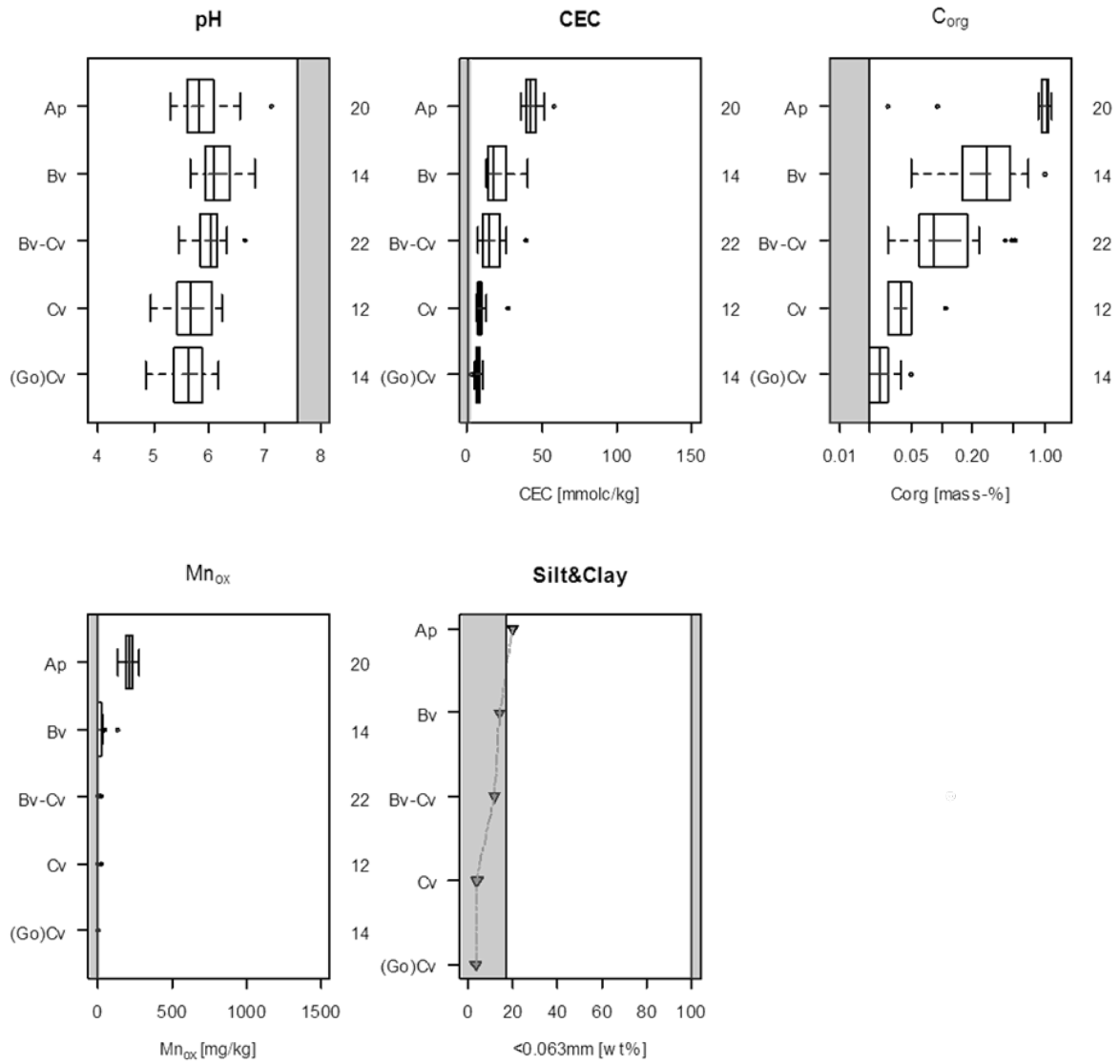


Figure 15: Basic soil properties in a gleyic cambisol. CEC: cation exchange capacity, C_{org}: organic carbon, Mn_{ox}: oxalate extractable Mn, numbers on the right hand y axis of the plots represent the sample sizes, width of the horizontal line through the median represents the CI ($\alpha = 0.1$) of the median, in orders of magnitude

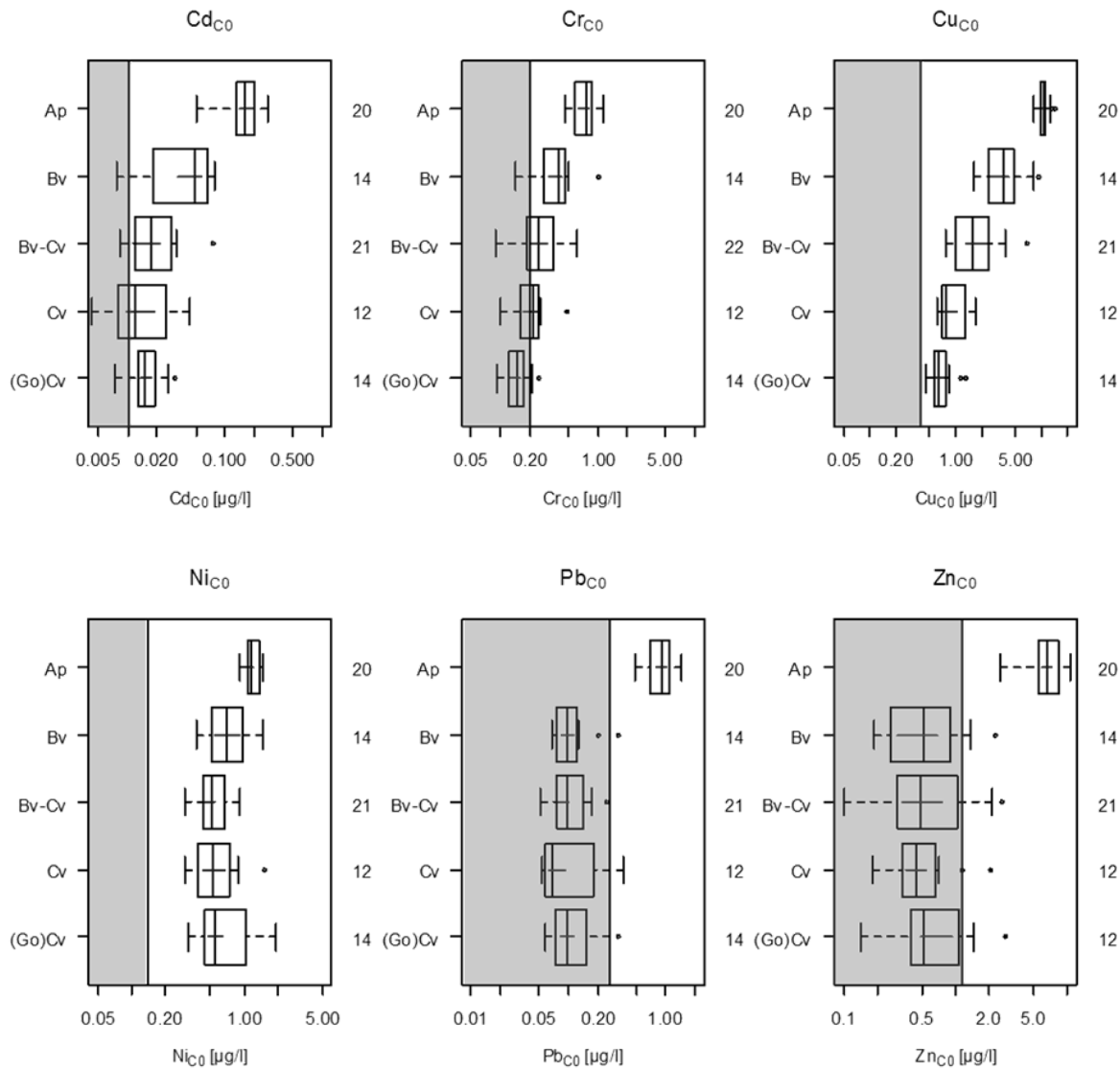


Figure 16: $\text{Ca}(\text{NO}_3)_2$ soluble concentrations of Cd, Cr, Ni, Pb and Zn in a gleyic cambisol. Numbers on the right hand y axis of the plots represent the sample sizes, width of the horizontal line through the median represents the CI ($\alpha = 0.1$) of the median, in orders of magnitude

In the haplic luvisol the pH value in some cases exceeded the maximum valid pH of the training data set. These samples were excluded from the database (Figure 17). All other soil properties considered as input variables were well within the range of validity. In the haplic luvisol in many horizons soluble trace element concentrations were smaller than the minimum valid concentrations in the training data sets. The silt and clay content of the sandy horizons were lower than in any of the soil used in the training data set.

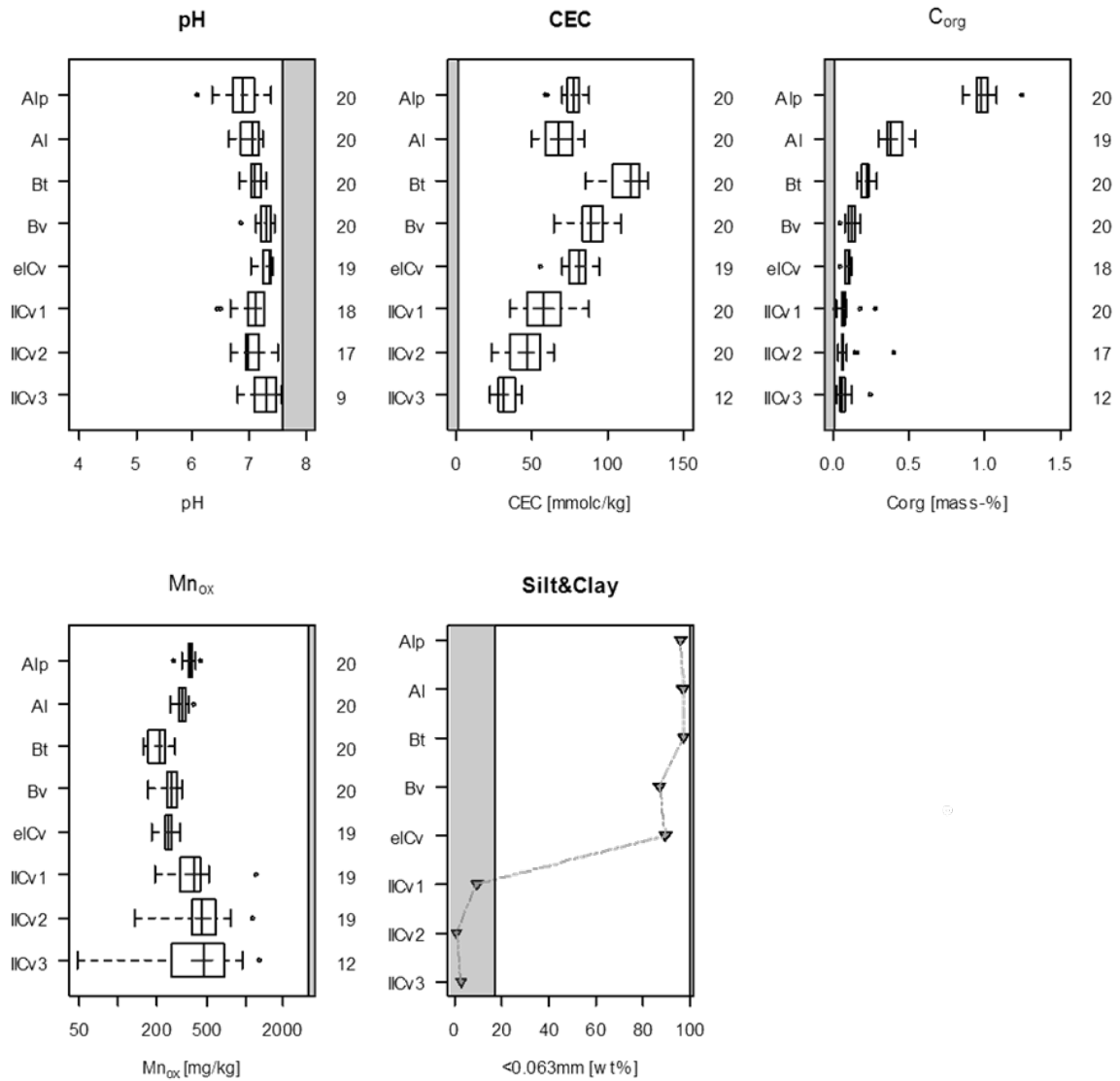


Figure 17: Basic soil properties in a haplic luvisol. CEC: cation exchange capacity, C_{org}: organic carbon, Mn_{ox}: oxalate extractable Mn, numbers on the right hand y axis of the plots represent the sample sizes, width of the horizontal line through the median represents the CI ($\alpha = 0.1$) of the median, in orders of magnitude

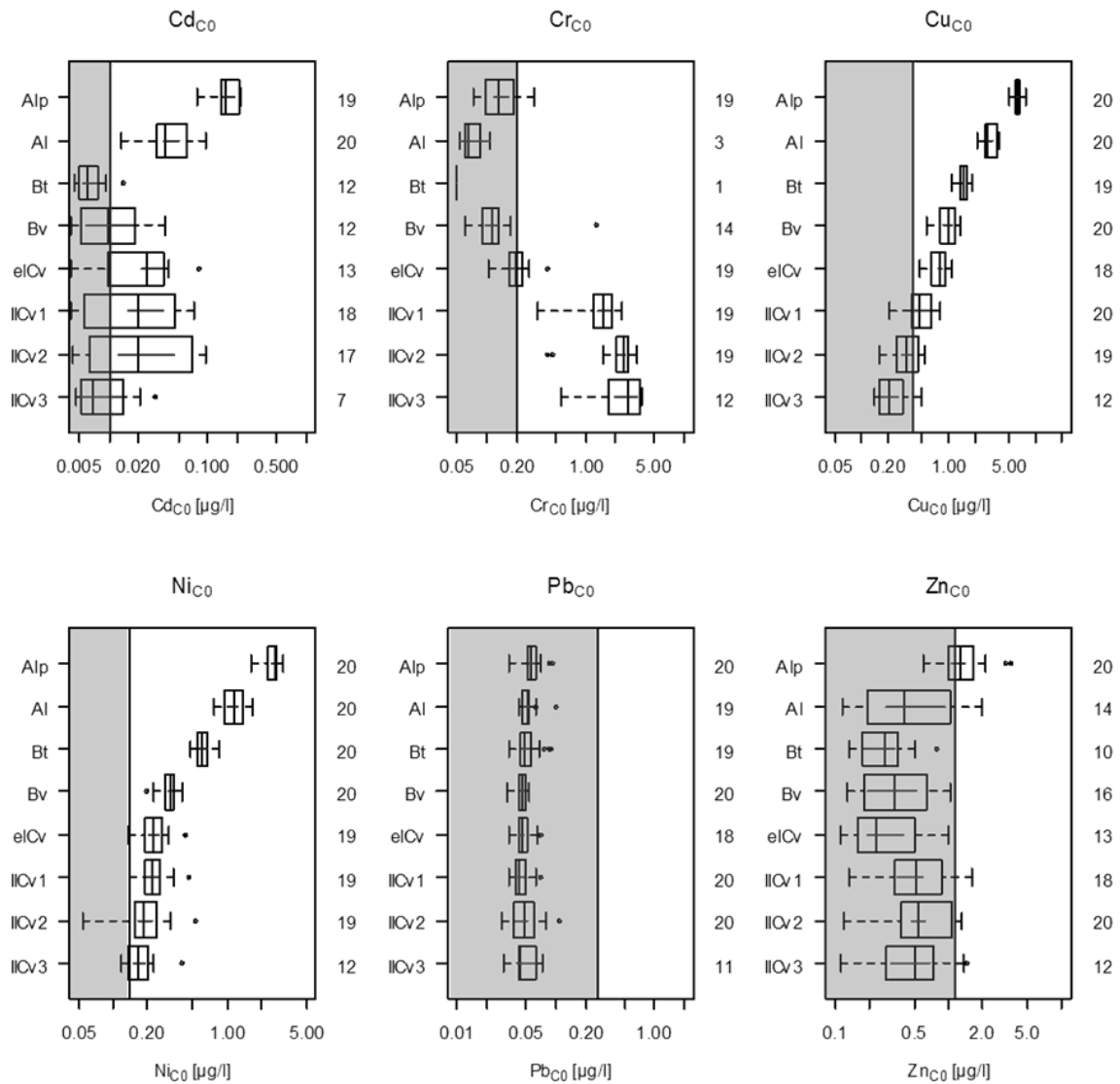


Figure 18: $\text{Ca}(\text{NO}_3)_2$ soluble concentrations of Cd, Cr, Ni, Pb and Zn in a haplic luvisol. Numbers on the right hand y axis of the plots represent the sample sizes, width of the horizontal line through the median represents the CI ($\alpha = 0.1$) of the median, in orders of magnitude

The natural variability examined in this study was solely due to spatial variability since all samples were collected within a day. This study neglected the aspect of temporal variability. For practical risk assessment issues temporal variability should be taken into account, because throughout a year concentrations of trace elements in percolation water can alter significantly (Bielert 1999).

The distance between the 1st and 3rd quartile (IQD) quantifies the spatial variability. Confidence intervals (CI, $\alpha = 0.1$) of the median show the range of concentrations in which with a probability of 90% the true median is probably located. The width of CI is a quantifier for the uncertainty of the median. We calculated all measures of uncertainty for every horizon. Measures of uncertainty are given for real and log-transformed data (Table 12). From one

horizon to another soil properties and concentration levels can change drastically. By showing measures of uncertainty \log_{10} -transformed data we are able to compare the uncertainty of different horizons independent of the underlying concentration level.

Table 12: Summary of the uncertainty of input variables, IQD: inter quartile range, CI: nonparametric bootstrap percentile confidence interval of the median ($\alpha = 0.1$)

cambisol		IQD		CI	
		mean (minimum, maximum)	\log_{10} mean (minimum, maximum)	mean (minimum, maximum)	\log_{10} mean (minimum, maximum)
pH			0.60 (0.28, 1.39)		0.34 (0.18, 0.63)
CEC	[mmol _c /kg]	5.8 (1.06, 12.09)	0.13 (0.06, 0.28)	3.9 (0.46, 9)	0.11 (0.03, 0.2)
C _{org}	[% w/w]	0.09 (0.01, 0.27)	0.22 (0.05, 0.45)	0.05 (0, 0.1)	0.13 (0.04, 0.34)
Mn _{ox}	[mg/kg]	9.49 (0, 37.55)	0.37 (0, 1.57)	6.26 (0, 24.79)	0.28 (0, 1.42)
Cd	[µg/l]	0.03 (0.01, 0.07)	0.37 (0.16, 0.52)	0.02 (0, 0.05)	0.25 (0.12, 0.44)
Cr	[µg/l]	0.18 (0.04, 0.33)	0.22 (0.12, 0.4)	0.12 (0.03, 0.25)	0.16 (0.09, 0.31)
Cu	[µg/l]	1.02 (0.21, 2.22)	0.22 (0.06, 0.4)	0.69 (0.12, 1.7)	0.14 (0.03, 0.26)
Ni	[µg/l]	0.46 (0.23, 0.84)	0.27 (0.11, 0.41)	0.26 (0.09, 0.62)	0.16 (0.04, 0.3)
Pb	[µg/l]	0.13 (0.04, 0.38)	0.30 (0.18, 0.6)	0.06 (0.02, 0.2)	0.15 (0.09, 0.34)
Zn	[µg/l]	0.92 (0.3, 2.73)	0.38 (0.18, 0.53)	0.54 (0.18, 1.25)	0.27 (0.08, 0.37)
Luvisol					
pH			0.25 (0.09, 0.45)		0.15 (0.04, 0.32)
CEC	[mmol _c /kg]	13 (7, 20)	0.10 (0.04, 0.19)	8.4 (4.45, 13.45)	0.06 (0.02, 0.1)
C _{org}	[% w/w]	0.05 (0.02, 0.12)	0.15 (0.03, 0.33)	0.03 (0.01, 0.1)	0.09 (0.02, 0.26)
Mn _{ox}	[mg/kg]	164 (23, 637)	0.17 (0.03, 0.55)	87 (13, 304)	0.09 (0.02, 0.28)
Cd	[µg/l]	0.03 (0, 0.07)	0.47 (0.15, 1.05)	0.02 (0, 0.05)	0.29 (0.13, 0.53)
Cr	[µg/l]	0.55 (0, 1.86)	0.18 (0, 0.32)	0.36 (0, 1.3)	0.16 (0.08, 0.29)
Cu	[µg/l]	0.34 (0.1, 0.88)	0.18 (0.05, 0.32)	0.18 (0.07, 0.4)	0.11 (0.02, 0.25)
Ni	[µg/l]	0.14 (0.04, 0.41)	0.12 (0.07, 0.19)	0.08 (0.02, 0.22)	0.08 (0.03, 0.11)
Pb	[µg/l]	0.012 (0.01, 0.02)	0.12 (0.06, 0.22)	0.009 (0, 0.02)	0.09 (0.04, 0.22)
Zn	[µg/l]	0.47 (0.17, 0.79)	0.41 (0.2, 0.67)	0.29 (0.14, 0.65)	0.27 (0.11, 0.52)

Measures of uncertainty in real concentration levels enable us to appreciate the different magnitudes of uncertainty. Table 12 shows the smallest, largest and the average of the spatial variability (IQD) and uncertainty of the median (CI of the median) of input parameters of both soils. This aggregated form of presentation allows us to comfortably compare the uncertainty of one soil with the other.

The uncertainty of the single value and uncertainty of the median of almost all parameters were smaller in the cambisol than in the luvisol. For Cr absolute IQD and CI are larger in the cambisol. In the luvisol, the range between minimum and maximum spatial variability and uncertainty of the median was wider than in the cambisol (Table 12). The average spatial variability of Cd, and Zn which occur in a similar concentration level in both soils, was higher in the cambisol. The average uncertainty of the median was similar for Cd and Zn, and smaller for other elements in the cambisol. In the luvisol trace element concentrations in percolation water were often smaller than or slightly larger than the limit of quantification. These additional analytical uncertainties may be the reason for the increased uncertainty of the median of many trace element concentrations in the luvisol.

4.4.2 Uncertainty of predicted S0 trace element concentrations

We used the general purpose PTF (Equations 7 and 8), trace element concentrations in aqueous extracts with adjusted ionic strength and soil properties $v_i = (c(H^+)_i, CEC_i, C_{org\ i}, Mn_{ox\ i}, C_i)$, to predict sorbed trace element concentrations S0. In order to avoid masking spatial variability with uncertainty of the median and vice versa (Heuvelink and Pebesma 1999), we strictly applied the PTF on a point support. Uncertainty of the single S_{PTF} prediction, quantified by the inter quartile range IQD of $N \leq 20$. The confidence interval of a horizons median of predicted S0 concentrations is a measure for the uncertainty of the median.

Spatial variability

Expressed in orders of magnitude the IQD were usually wider for predictions made for the cambisol as those of the predicted solid phase concentrations of the luvisol (Table 13). For the latter Cd and Zn showed the highest spatial variability. The predictions made for the cambisol were, except for Pb, less spatially variable than their measured equivalents, whereas in the luvisol the predicted values were typically more variable than the measured ones.

The analytical uncertainty may have been the source of increased variability and not the true spatial variability.

Table 13: Summary of the uncertainty of the predicted solid phase trace element concentrations [\log_{10} $\mu\text{g}/\text{kg}$] in comparison to the uncertainty of EDTA-extractable trace element concentrations (suffix "EDTA"), in orders of magnitude, IQD: inter quartile range, CI: nonparametric bootstrap percentile confidence interval of the ($\alpha=0.1$), model error; difference between predicted solid phase trace element concentrations $S_{0\text{PTF}}$ and Na_2 -EDTA-extractable solid phase trace element concentrations $S_{0\text{EDTA}}$

Cambisol	IQD		CI		model error ($\log S_{0\text{PTF}} - \log S_{0\text{EDTA}}$)
	mean (minimum, maximum)	mean _{EDTA}	mean (minimum, maximum)	mean _{EDTA}	mean (minimum, maximum*)
Cd	0.31 (0.12, 0.61)	0.36	0.20 (0.06, 0.43)	0.28	0.30 (0.01, 0.71)
Cr	0.18 (0.1, 0.32)	0.22	0.13 (0.07, 0.25)	0.13	0.76 (0.25, 1.25)
Cu	0.31 (0.11, 0.53)	0.46	0.20 (0.06, 0.35)	0.31	0.28 (0.11, 0.57)
Ni	0.21 (0.11, 0.36)	0.15	0.13 (0.04, 0.25)	0.11	0.18 (0, 0.33)
Pb	0.40 (0.23, 0.64)	0.17	0.22 (0.09, 0.35)	0.11	0.12 (0.01, 0.26)
Zn	0.29 (0.08, 0.45)	0.37	0.18 (0.03, 0.27)	0.28	0.25 (0.03, 0.54)
Luvisol					
Cd	0.35 (0.14, 0.56)	0.20	0.24 (0.1, 0.47)	0.13	0.35 (0.08, 0.78)
Cr	0.15 (0, 0.26)	0.13	0.11 (0, 0.23)	0.09	0.97 (0.01, 2.09)
Cu	0.16 (0.08, 0.25)	0.20	0.10 (0.04, 0.2)	0.14	0.30 (0.07, 0.51)
Ni	0.14 (0.06, 0.24)	0.20	0.08 (0.03, 0.11)	0.13	0.87 (0.06, 1.63)
Pb	0.13 (0.07, 0.24)	0.09	0.08 (0.03, 0.13)	0.05	0.33 (0.1, 0.61)
Zn	0.22 (0.08, 0.4)	0.24	0.14 (0.04, 0.27)	0.14	0.69 (0.04, 1.34)

* the smallest respectively largest medians of model errors calculated per horizon

Informational sources of uncertainty

Uncertainty of the measure of central tendency

The uncertainty of the median of the predictions (CI of $S_{0\text{PTF}}$) was slightly smaller in the luvisol than in the cambisol (CI in Table 13). As the uncertainty of the median of the input variables in the luvisol was also smaller than in the cambisol, the higher level of uncertainty propagated through the PTF. Typical uncertainty of the median S_0 prediction calculated from

$N \approx 20$ ranged between 0.08 and 0.22 orders of magnitude. Even in horizons with small sample sizes ($N < 10$) CI did not exceed 0.47 orders of magnitude (Table 13).

In the cambisol the uncertainty of the median of $S_{O_{PTF}}$ was often smaller than the uncertainty of the median of $S_{O_{EDTA}}$ (Table 13). Since the Na_2 -EDTA extractable trace element concentrations in the cambisol were close to the limit of quantification increased analytical uncertainty may have been the source of the higher uncertainty of the median of the measured concentrations. Since the CO concentration in the luvisol were very low and often close to the limit of quantification, this increase uncertainty may have manifested itself in the larger variability and uncertainty of the median of the predicted values compared to the variability of the measured values.

Model error

The difference between predicted S_0 and trace element concentrations in Na_2 -EDTA, both \log_{10} -transformed, quantifies the model error. We used log transformed concentrations to be able to compare model errors of different concentration levels with each other. To quantify the average uncertainty of the PTF predictions for a given horizon, we used the median model error per horizon (Table 13). Utermann et al. (2005) did not estimate error terms for their PTFs. Heidkamp (2005) derived PTF for soils used for forestry using a very similar approach and sample size and regional distribution. He defined the 95% confidence interval of \log_{10} residuals as an error term $\log_{10} \epsilon$. For his PTF he reported $\log_{10} \epsilon$ from ± 0.36 up to ± 0.68 orders of magnitude (Heidkamp 2005). In the plots showing the model error (Figure 19 and Figure 20) we marked, based on Heidkamps (2005) findings, ± 0.5 orders of magnitude with dashed lines as an orientation for an acceptable size of model error.

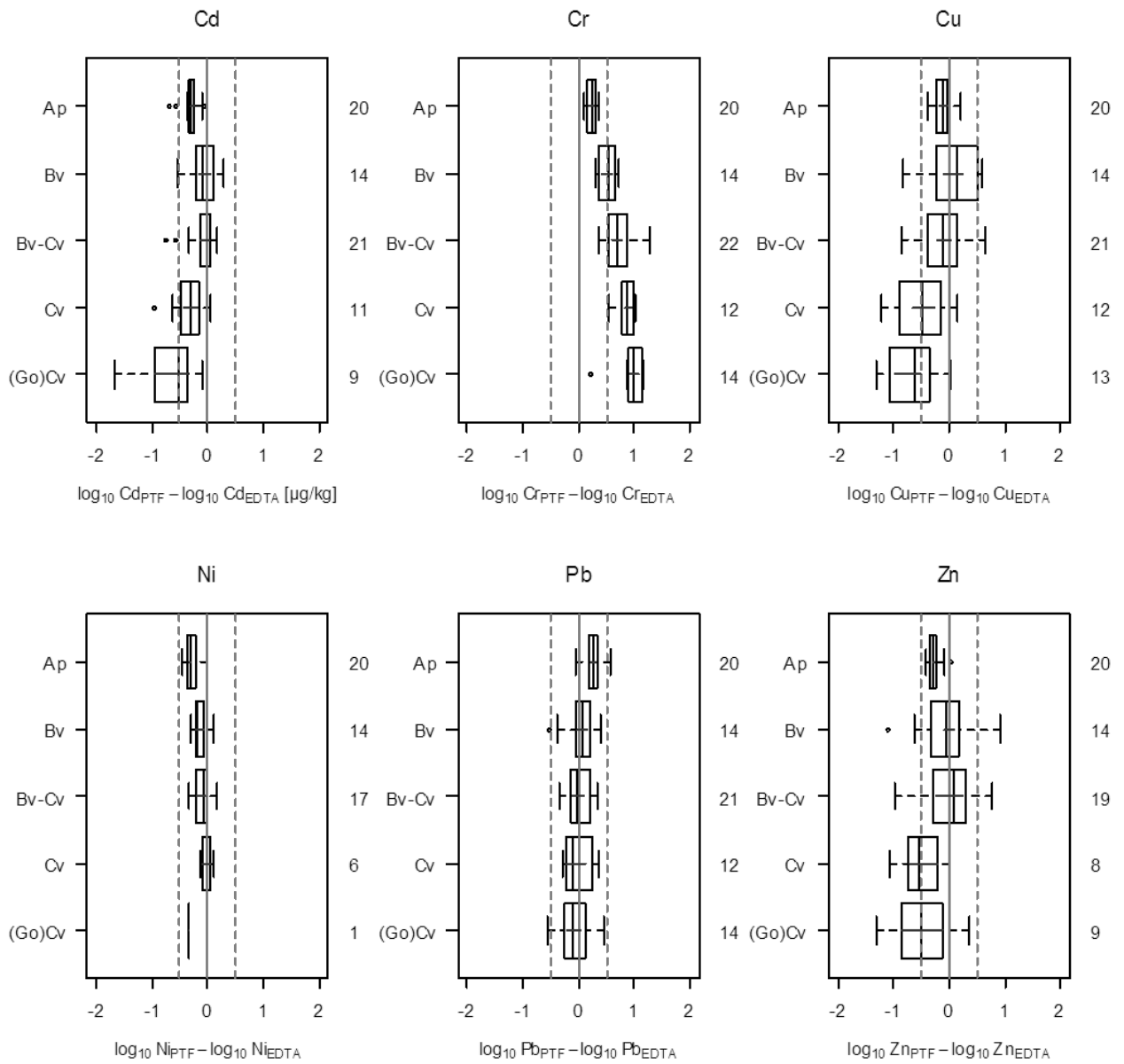


Figure 19: Model error of PTF predicted solid phase concentrations of Cd, Cr, Ni, Pb and Zn in a gleyic cambisol. Numbers on the right hand y axis of the plots represent the sample sizes, width of the horizontal line through the median represents the CI ($\alpha = 0.1$) of the median, in orders of magnitude

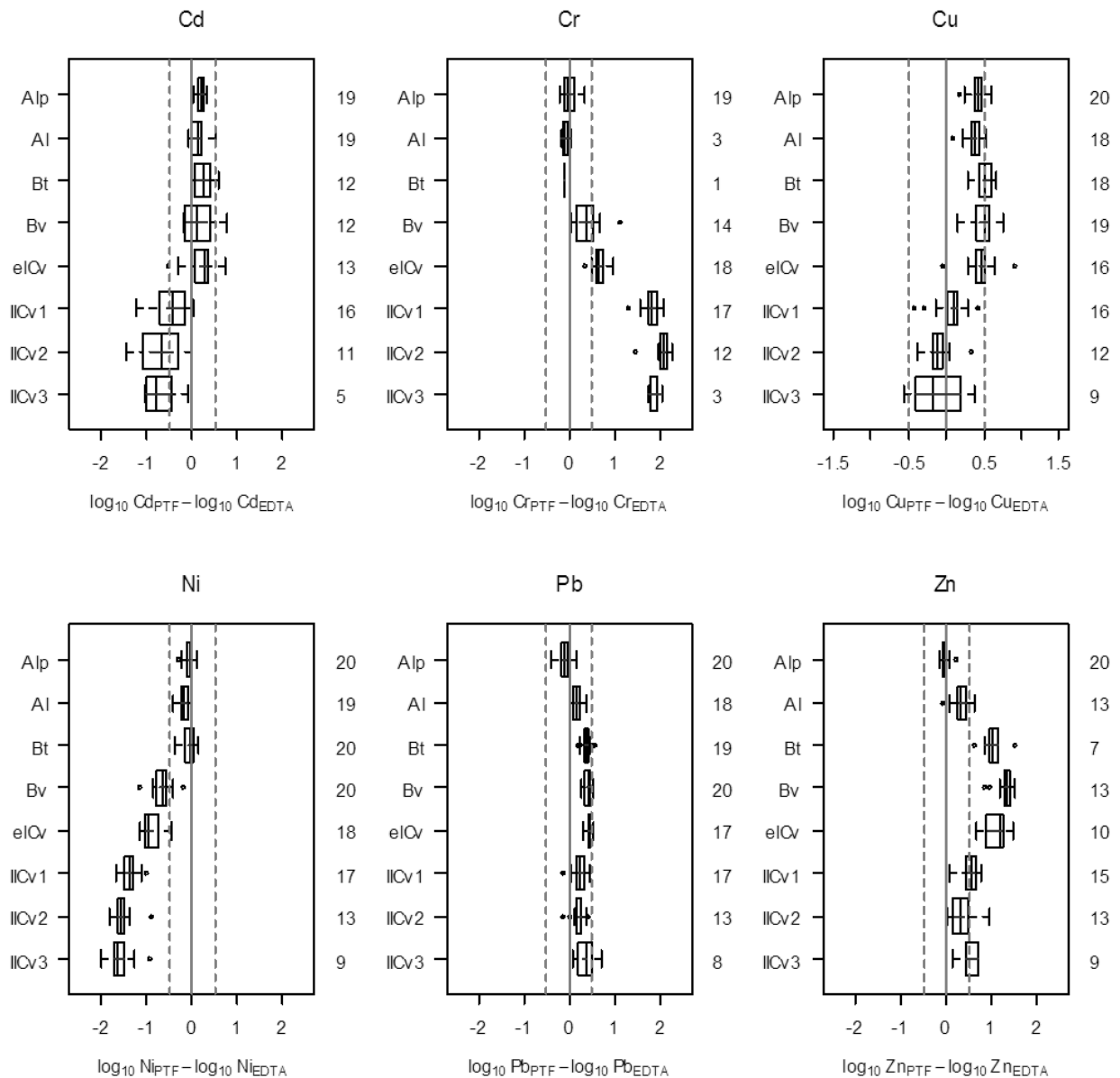


Figure 20: Model error of PTF predicted solid phase concentrations of Cd, Cr, Ni, Pb and Zn in a haplic luvisol. Numbers on the right hand y axis of the plots represent the sample sizes, width of the horizontal line through the median represents the CI ($\alpha = 0.1$) of the median in orders of magnitude

The magnitude of the model error ($\log_{10} S_{O_{PTF}} - \log_{10} S_{O_{EDTA}}$) in the prediction of the solid phase concentrations of Cd, Cr, Ni and Zn was variable. Therefore in Figure 19 and Figure 20 the model error is shown in form of box plots for every horizon.

In the luvisol the predictions made for the loamy part of the soil were usually more accurate than those made for the sandy part. The Cd model errors of the loamy part of the luvisol were smaller 0.5 orders of magnitude, but showed a trend for overestimation. In the sandy layer of the luvisol the model error was often greater than 0.5 orders of magnitude. The prediction of Cr concentrations worked well for the first two horizons of the luvisol. In the

sandy horizons the model error for Cr predictions gradually increased with increasing depth and increasing sand content in the soil texture. A similar pattern with similar uncertainty of the median model error but with generally higher variability was observed for predictions of Cr in the cambisol cambisol. Since the predictions of SO concentrations of Cr solely rely on the CO concentrations, the similarity of soil properties of soil samples the centre of the training dataset to the soil samples in question is of vital importance. In the training dataset of Utermann et al. (2005) sandy soil were underrepresented. The highest sand content of samples from the training dataset was 83%, whereas in the soils studied in this work the median sand content of the sandy soils was between 91% and 99.5% (luvisol) respectively 80% and 97% (cambisol). The assumption that the reason for the low accuracy of the PTF for Cr can be attributed to the low clay contents, is supported by the finding that the model error of Cr showed a significant negative correlation with the content of silt and clay particles $< 63\mu\text{m}$ (spearman- ρ -0.64 calculated from $N = 113$ samples).

Neutral to alkaline pH values in the luvisol may have been another key source of model error. In this pH range the sorption processes get increasingly complex because the solubility of some sorption relevant properties such as Mn_{ox} or C_{org} is affected in addition to the trace elements solubility. As a result Staunton (2004) reported non-linear changes in the partition relations between the solid phase and soluble concentrations of Ni. At about pH 6.5 the slope characterizing the partition relation suddenly increased showing a quicker increase of sorption capacity from that point on until the sorption capacity started to decrease from about pH 7.6. The sudden stronger increase in sorption capacity in relation to the pH value can roughly also be observed in our data of the luvisol. Since this non-linear increase in sorption capacity was not captured by the extended Freundlich equation, the result was an underestimation of solid phase concentrations of Ni, although pH values were within range of validity.

A related but opposite phenomenon may explain the model error which occurred for Zn in horizons with higher pH values. Results of a pH-stat test showed a change of decreasing to increasing solubility of Zn with increasing pH at about pH 7 (Groenenberg 2011). A similar abrupt increase of solubility, or phrased in our terms, decrease of sorption capacity may have been the reason for the distinct overestimation of Zn in the Bt, Bv, eCv and IIC horizons, which were the horizons with the highest pH values. Here too the log-linear model of the Freundlich equation was incapable to mirror this change in sorption behaviour.

It is also possible that the model error of Zn predictions was due to the choice of extracting agent. The PTF failed to correctly predict SO concentrations of Zn in the Bt, Bv and eICv horizons and overestimated SO other elements such as Cd, Cu and Pb in these horizons. These horizons were especially rich in calcium carbonate. The extracting agent Na₂-EDTA was less effective on calcareous materials, because concurrent extraction of Ca can consume up to 90% of the chelating agent Na₂-EDTA (Pappasiopi 1999). The PTF derived by Utermann et al. (2005) is based on SO data where the potentially exchangeable fraction is estimated by isotope dilution mass spectrometry. This method is very specific for the element in question (Gäbler 2007). The hindered effectiveness of Na₂-EDTA in calcareous materials was thus not mirrored in the PTF. In this case the PTF prediction may have actually represented the current amount of potentially exchangeable trace elements more accurately than Na₂-EDTA extraction.

Concentrations of trace elements lower than the lower limit of validity did not systematically increase the model error. CO concentrations of Pb in the luvisol were without exception smaller than the minimum concentrations in the training dataset of Utermann et al. (2005). Still, the PTF for Pb concentrations predicted with small error (< 0.5) Predicting Pb concentrations worked also well for the cambisol (Figure 19), although here too the CO concentrations were mostly smaller than the minimum of the training data set. Though inhibiting a larger spatial variability than in the luvisol, the CI of the model error touched the 0-errormark, suggesting that respecting uncertainty of the median the model error may be random.

The magnitude of the model error found in this study is in accordance with findings from other authors. Elzinga et al. (1999) tested various Freundlich equation based PTF for the prediction of solid phase concentrations and found even larger model errors for concentration levels equivalent to the solid phase concentrations assessed in this study. The average model error observed in their study gradually decreased with increasing concentration level. For a concentration range of 0 - 600 µg/kg Cd they reported that concentrations were in average overestimated by 1.2 orders of magnitude. The model error thereby showed a wide range (10th percentile 0.4 orders of magnitude, 90th percentile 1.7 orders of magnitude). For predictions made for solid phase Zn concentrations ranging between 10 and 9600 µg/kg they reported an average model error of 0.5 orders of magnitude.

Predictions made for low solid phase Cu concentrations (100 - 18000 µg/kg) were inclined by model errors ranging from -0.04 to 1.9 orders of magnitude (Elzinga et al. 1999).

The high spatial variability of the model error for Zn and Cu were probably caused by the high or very high spatial variability of the Na₂-EDTA-extractable solid phase concentrations. Whether this was a true spatial variability or includes additional sources of uncertainty remains to be studied. Since the Na₂-EDTA-extractable solid phase concentrations were very close to the limit of quantification it is not at all unlikely that some of the variation was caused by analytical error that propagates through to the model error. This could also explain why the predicted solid phase concentrations in the cambisol were less variable than the measured values.

4.4.3 Relative importance of different sources of uncertainty

The relative importance of different sources of uncertainty accompanied with predicted S0 trace element concentrations within one horizon is shown in Figure 21 and Figure 22. With sample sizes of N = 10 - 20 the uncertainty of the median (CI of the median) was always smaller than uncertainty of the single value. The median of N ≥ 10 samples is likely to be less uncertain than the single value.

S0 predictions made for topsoil horizons were accompanied with the smallest uncertainty relatively to the concentration level. The largest contributor to the uncertainty of S0 predictions in the topsoil horizon of the cambisol was the model error followed by the spatial variability. In the topsoil horizon of the luvisol the main source of uncertainty was the spatial variability except for S0 predictions of Cd and Cu, whose uncertainty was mostly a result of model error. The total uncertainty varied between 0.15 (Zn) and 0.61 (Cu) orders of magnitude.

In the subsoil horizons the total uncertainty was mostly caused by larger model errors. The uncertainty within subsoil horizons was usually largest for predictions made for Cr, whereupon the informational uncertainty in consequence of the large or very large model error was the predominant source of uncertainty. In the cambisol the uncertainty in S0 predictions of other trace elements for subsoil horizons was mostly due to the spatial variability. In the luvisol S0 predictions made for Ni and Pb were accompanied with the smallest amount of uncertainty. In subsoil horizons of the luvisol the model error exceeded all other sources of uncertainty. Considering the three sources of uncertainty individually, for S0 predictions of Cd the spatial variability, represented by the IQD, was the major source of uncertainty.

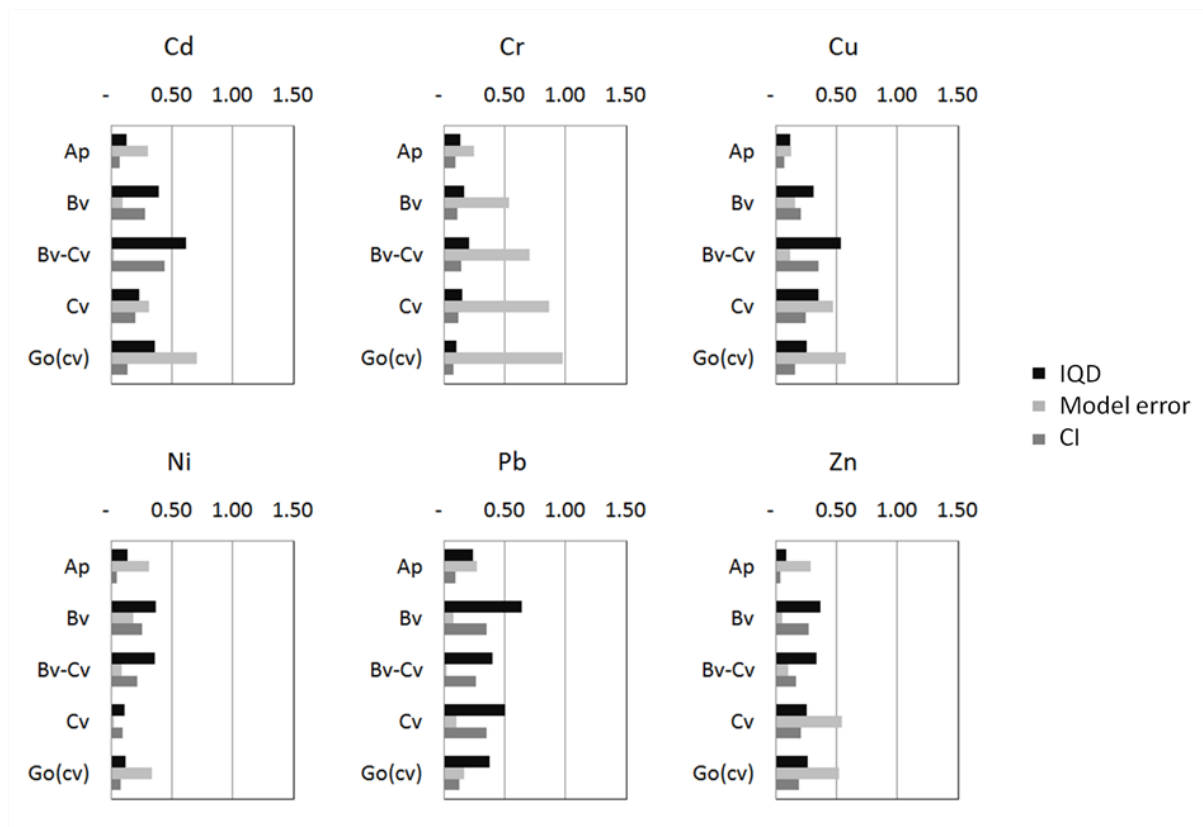


Figure 21: Relative importance of spatial variability (represented by inter quartile distance IQD), model error and uncertainty of the median (represented by CI ($\alpha = 0.1$) of the median PTF predicted concentrations of potentially exchangeable trace elements) within horizons in a gleyic cambisol, in orders of magnitude

The absolute magnitude of the spatial variability was related to the concentration level whereas the model error was mostly related to the soil properties. Thus, for a successful prediction validity of the basic soil properties was more important than valid concentration levels of soluble trace elements. A lower trace element concentration does not change the processes governing equilibrium. Exceedance of physicochemical soil properties beyond a physicochemical threshold of validity on the other hand does result in structural changes in the sorption or desorption processes and/or kinetics, as the above discussed influence of the pH value showed. Consequently, the model error was more sensitive toward invalidity of physicochemical soil properties than toward trace element concentrations deceeding the range of validity.

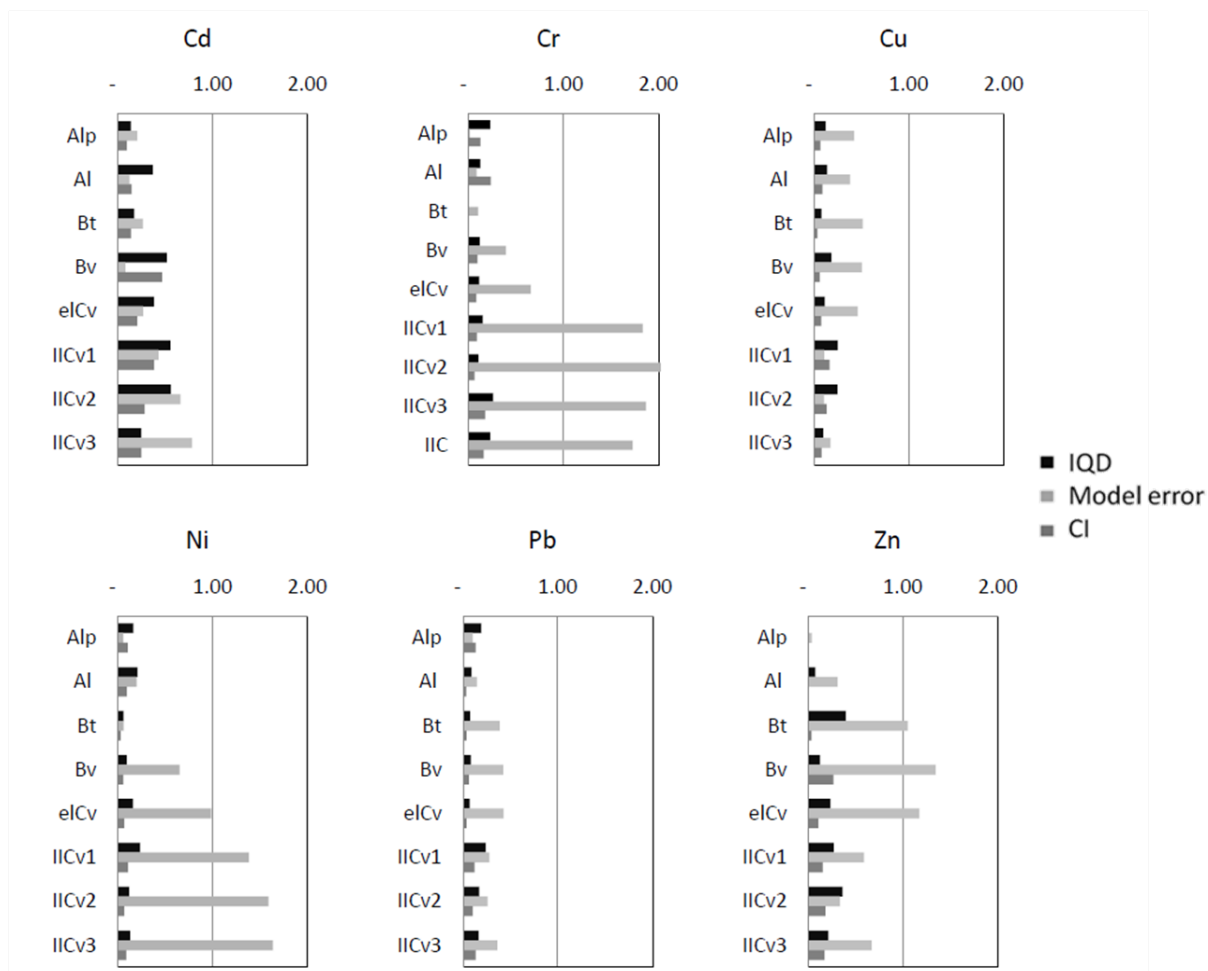


Figure 22: Relative importance of spatial variability (represented by inter quartile distance IQD), model error and uncertainty of the median (represented by CI ($\alpha = 0.1$) of the median PTF predicted concentrations of potentially exchangeable trace elements) within horizons in a haplic luvisol in orders of magnitude

4.5 Conclusions

We found model error the predominant source of uncertainty in soils with $\text{pH} > 6.5$. Based on our findings we conclude that the PTF used to predict S_0 (Utermann et al. 2005) are in cases where adsorption is the key mechanism of trace element retention a fairly reliable tool to estimate solid phase concentrations of trace elements when uncertainty of up to 0.5 order of magnitude is acceptable. This is also true for very low trace element concentrations below the original range of validity. For soils where adsorption is the key retention mechanism the main source of uncertainty is the natural variability of the governing soil parameters. The PTF for Cr has to be excluded from this statement because the model error was the predominant source of uncertainty in nearly all horizons and soils. Based on this uncertainty analysis we discourage the application of Cr PTF from Utermann et al. (2005) on sandy soils. Additionally we advise against applying Ni and Zn PTF on soils with $\text{pH} > 6.5$.

The uncertainty analysis has shown that the general purpose pedotransfer functions were more sensitive toward invalidity of physicochemical soil properties than toward invalidity of trace element concentrations in low concentrations.

Predictions made for topsoil horizons were relative to the concentration level accompanied by a smaller uncertainty than predictions made for subsoil horizons. Typical uncertainty of single SO predictions based on general purpose PTF by Utermann et al. (2005) made for topsoil horizons with N = 20 samples ranged from 0.08 to 0.23 orders of magnitude. The average total uncertainty of PTF predictions made for subsoil horizons varied from 0.06 to 0.64 orders of magnitude.

Decision makers should be informed that a uncertainty of the median of 0.1 - 0.2 orders of magnitude and an uncertainty of the single prediction of 0.1 - 0.6 orders of magnitude has to be expected for PTF predicted trace element concentrations. In addition a model error of 0.2 - 0.3 orders of magnitude has to be expected independent of the concentration level even in soils where adsorption is the key retention mechanism and soil properties are well within the range of validity.

4.6 References

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5 Final Results and Discussion

5.1 Spatial variability

The spatial variability of trace element concentrations in percolation water was mostly dependent on the spatial variability of pH and dissolved organic carbon (DOC) concentrations. The results in Chapters 2, 3 and 4 showed that mobility, and thus the spatial distribution, were mostly affected by pH and DOC concentrations. In the stepwise multiple regression analysis conducted in Chapter 2, the physicochemical soil properties pH, DOC, organic carbon C_{org} , cation exchange capacity CEC, oxalate soluble iron Fe_{ox} and manganese Mn_{ox} and Na_2 -EDTA extractable trace element concentration were offered as independent variables. The regression models with the highest determination coefficient to explain the soluble trace element content of either Cd, Zn, Mo Pb, Co or Ni included pH as the first input variable. The regression models aiming to explain soluble concentrations of As, Cu, V, Cr, Sb or Zn in percolation water showed the highest determination coefficient when DOC was included as first input variable. Increased concentration of DOC reduces the retention of otherwise strongly bound ions in small concentrations (Goody et al. 1995). The effect of DOC on the mobility of trace elements seems to be especially effective in low trace element concentrations (Goody et al. 1995). Trace element concentrations in the collection of samples were at background concentration levels. The combination of low concentration levels and the high percentage of sandy soils with small sorption capacities may explain the predominant role of DOC as a major governing factor for the variability of trace element concentrations. The importance of pH as a governing factor for the mobility of trace elements and its consequence for trace element variability has already been established in various studies (e.g. Sposito 1998, Adriano 2001 or Harter and Naidu 2001). Because variations in pH and DOC correlate with variations in trace element concentrations, the uncertainty of background values due to variability of background concentrations can be reduced by stratification in classes of high and low pH values and high and low DOC concentrations.

Nevertheless, the variability of trace element concentrations within a group of similar pH or DOC concentrations was still considerable. The IQD of trace element concentrations in percolation water within one class was on average as wide as 0.5 - 1 in order of magnitude (Figure 6 and Figure 7 in Chapter 2). Species combination and local stand density in forests can affect physicochemical properties of the soil (Silvia and Rodríguez 2001, Paluch and Gruba

2012). Amongst other soil properties, on arable land crop the choice of fertilizer or tillage routine affect C_{org} content and pH values (Tarkalson et al. 2006). The resulting heterogeneity of physicochemical soil properties was reflected in the variability of dissolved trace element concentrations within groups of similar pH or DOC concentrations. The soil properties affecting the solubility of trace elements varied according to land use and parent material. Stratification of background concentrations of trace elements according to parent material and land use also made it possible to reduce uncertainty and thus increase the representativeness of background values. Parent material and land use have formed the basis for the spatial representativeness for point data in attempts to illustrate the distribution of trace elements in European soils (European Soil Bureau-Scientific Committée 1999, LABO 2003). On arable land, the content of organic carbon and pH values are manipulated in order to achieve the best possible plant nutrition. Soil acidity manages to yield a pH of 5.5 - 6.5. Legislation and agricultural advisory services across Germany and Europe aim to achieve a consistently high C_{org} content in the topsoil of arable land. Long-term land use as forest, especially under conifers, results in an increasing acidification of soils. Soils which are too wet for arable land are often used as grassland. High biomass production and incomplete decomposition on such sites increases DOC concentration in the percolation water. High DOC concentration in percolation water promotes increased mobility of trace elements with an affinity for metal-organic complexes (Goody et al. 1995). The effects of land use on the concentrations of trace elements are most visible in percolation water from soils generated from sand parent material which has a low sorption and buffer capacity (Duijnsveld et al. 2008). Thus, by stratifying according to land use and parent material or spatial representativeness, the precision of background values can be increased.

A large portion of the variability of trace element concentrations in percolation water was found within the field scale. In extreme cases, the concentration range within one field was as wide as the spatial variability within a parent material and land-use group (Duijnsveld et al. 2008). On average the field scale variability in this study was 17 to 37% of the regional scale variability resulting in an average field scale IQD of orders of magnitude of 0.22 to 0.42. Other studies report similar phenomena for field scale variability of soil properties and trace element concentrations in soil and percolation water. The highest degree of variance in As, Cd, Cu, Pb, Sb and Zn concentrations in soils was found at distances smaller than 300 m (Spijker et al. 2005). Altfelder et al. (2007) found local scale (< 100 m) variability in trace element

concentrations of one to two orders of magnitude. At distances greater than 300 m, variability still increased, albeit to a lesser extent (ibid.). Dahiya et al. (1984) reported that, although the rule that the variability of soil properties increases with scale still holds, most variability could be found within several metres. Garten et al. (2007) discovered that the spatial variability of soil properties, such as organic carbon concentrations, was as variable at small scales (1 - 10m) as it was at scales of 50 - 500 m. It is important to recognize the high degree of spatial variability within short distances because – in contrast to other sources of uncertainty – it is not reducible.

5.2 Informational sources of uncertainty

5.2.1 Uncertainty of the median

Although field scale variability was not the largest source of uncertainty (Table 14), it still significantly affected the influence of central estimates in the field scale. The pronounced variability of trace element concentrations at field scale impeded the applicability of insignificance thresholds there. Spatial variability reduced the ability of single values to characterize the site, as well as the precision of measures of central tendency. Due to the spatial variability of soils and the resulting variability in trace element concentrations in the percolation water, statements could only be made with acceptable statistical uncertainty ($\alpha \leq 0.1$) concerning exceedance or nonexceedance of GFS values when operational median ($N \leq 10$) concentrations (i.e. the estimated median on site) were approximately 1/3 higher or lower than their critical GFS (Chapter 2). Due to the high level of variability detected and in view of the resulting uncertainty, it is important to understand that exploratory investigations with sample sizes of $N \approx 10$ were only able to supply a qualitative orientation with respect to trace element status in percolation water, even when direct sampling of percolation water was used. Boekhold and van der Zee (1991) recommend taking soil heterogeneity into account when setting environmental quality standards, because even when average values suggest an acceptable situation, variability can still cause exceedance of operational concentrations in parts of the field. In order to allow the deciding body to judge the importance of results, degrees of uncertainty and variability should always be given. It is also important to clearly state the statistical method, i.e. statistical value for the central tendency, to allow the decider to reach a qualified judgment.

Table 14: Overview of uncertainty accompanying local estimates of trace element concentrations in percolation water, p = parametric, np = non-parametric, spatial variability: average of onsite IQD concentrations in orders of magnitude, Uncertainty of field scale median: average of nonparametric bootstrap percentile confidence intervals ($\alpha = 0.1$) calculated for onsite median of $N \leq 10$ samples, uncertainty of batch extraction: parametric confidence intervals ($\alpha = 0.1$) of single prediction from the comparison of concentrations in situ and in batch extracts

	Spatial variability	Uncertainty of the field scale median	Uncertainty of batch extraction	
	\emptyset onsite ($N \leq 10$) IQD	\emptyset onsite ($N \leq 10$) CI_{np} of median, $\alpha = 0.1$	LS 2 l/kg CI_p of residuals, $\alpha = 0.1$	LS 5 l/kg CI_p of residuals, $\alpha = 0.1$
As	0.29	± 0.28	± 0.42	± 0.44
Cd	0.40	± 0.37	± 0.71	± 0.66
Co	0.41	± 0.39	± 0.77	± 0.62
Cr	0.24	± 0.22	± 0.44	± 0.46
Cu	0.32	± 0.31	± 0.53	± 0.51
Mo	0.38	± 0.34	± 0.60	± 0.69
Ni	0.32	± 0.30	± 0.60	± 0.49
Pb	0.35	± 0.36	-	± 0.58
Sb	0.22	± 0.20	± 0.42	± 0.48
V	0.33	± 0.31	± 0.62	± 0.55
Zn	0.42	± 0.42	± 0.75	± 0.66

In Chapter 2, it has been shown that there is a strong relationship between the spatial variability quantified by the IQD and the confidence interval of the median. This finding suggests that a large share of the uncertainty for the median can be attributed to spatial variability. For $N \leq 10$ the average confidence interval (CI, $\alpha = 0.1$) of the median trace element concentration in percolation water was only marginally smaller than, in one case equal to and in the case of Pb even slightly larger than the average inter-quartile distance IQD (Table 14). This means that the median from $N \leq 10$ samples was only as precise as some 50% of onsite variability within a distance of 90 metres. Increasing the sample size will probably reduce the uncertainty of the median. In Chapter 4 the confidence intervals of median trace element concentrations based on $N \approx 20$ samples were as wide as 46% - 72% of the IQD. In a collaborative trial, Kurfürst et al. (2011) show that the width of a confidence interval of mean analyte mass fractions depends on the number of samples and on spatial variability. They show that on a field of “normal heterogeneity” (determination coefficient of approx. 40%) a narrow confidence interval of $\pm 10\%$ of the mean can only be achieved with high probability ($p = 0.9$) when $N \geq 37$ samples are used. It is however questionable whether in real life explorative investigations will ever yield as many as 10 samples per site.

5.2.2 Uncertainty from aqueous batch extraction

The precision and accuracy of the aqueous batch-extraction methods used in Chapter 3 was limited. Even the highest determination coefficients revealed that no more than 62% of the in situ concentration variance could be explained by the concentrations measured in the extracts (Table 7). This means that at least 38% of unexplained residual variance had to be expected when trace elements in batch extracts were used to estimate in situ concentrations. The imprecision of batch extracts was therefore quite large. Expressed in prediction intervals ($\alpha = 0.1$), characterizing the uncertainty of the single estimate, uncertainty due to imprecision was as great as 0.44 - 0.77 (Table 14). When using trace element concentration in extracts to characterize concentrations in situ, it also proved necessary to take account of the bias quantified in regression coefficient a and b over and above the residual variance. This led to uncertainties of one or two orders of magnitude when the in situ concentration was characterized by concentrations of batch extracts. Uncertainty due to systematic bias was quantifiable, and proved reducible to a certain degree by converting concentrations using the parameters shown in Table 7 in Chapter 3.

In the aforementioned comparison of concentrations of trace elements in batch extracts with concentrations in situ, cationic elements were usually estimated more accurately and often more precisely by batch extraction with adjusted ionic strength than without such an adjustment. For the liquid-solid ratio of 2 l kg⁻¹, the correlation between concentrations of a metal in the in situ soil solution and in the laboratory batch extract increased in the following order of sequence: Pb, Cr << As < Ni, Cu, Co, V, Zn, Mo, Sb < Cd. For the liquid-solid ratio of 5 l kg⁻¹, this order of sequence changed slightly to: Cr << As, Pb, Sb < Cu, Mo < V, Zn, Cd < Ni, Co. These results corresponded to the order of mobility of trace elements (Brümmer et al. 1986), with the least mobile elements showing the poorest correlation. For many elements the r^2 was similar for both extracts. Whenever there was a serious difference between the determination coefficients, the r^2 were usually higher for concentrations of cationic elements (such as Cd or Zn) measured in the liquid-solid ratio of 5 l kg⁻¹ extracts. The observations suggest that this increase was in part attributable to adjustment of the ionic strength, which led to pH values closer to in situ conditions. Adjustment of the ionic strength also led to a closer relationship between DOC concentrations in extract and in situ, which in turn resulted in a closer relationship between concentrations of elements known to build metal-organic complexes, such as V and Pb. Some aspects of the poor relationship were compre-

hensible when principal physicochemical processes were taken into consideration. In aqueous extracts with an ionic strength not adjusted to in situ conditions, dilution resulted in H⁺ concentrations almost three times lower than in situ (Table 8). Consequently cationic elements whose mobility was predominantly governed by pH were underestimated to some extent by extraction. Dilution and mechanical stress affected the solubility of organic carbon. DOC concentrations were on average five times higher than in situ in aqueous extracts without an additional background electrolyte. Increased DOC concentrations and pH values caused deviations of trace element concentrations in extracts from those in situ. By adjusting the ionic strength of the extracting agent to in situ conditions, the r^2 increased for all elements except As and Sb. Considerable increase (by more than 0.1) in determination coefficients was observed for Co, Cr, Ni, Pb, V and Zn. Consequently prediction uncertainty, expressed in confidence intervals ($\alpha = 0.1$) of the residuals, was lower for estimates based on extracts with adjusted ionic strength than for those without.

The experimental setups differed in more than one aspect, because the extraction methods were different both in solid solution ratio and ionic strength. It was thus not possible to fully comprehend the discrepancies between extract and in situ concentrations of trace elements. However, it was not the scope of this study to give a full understanding of processes leading to deviations between trace element concentrations in batch extracts and those in situ. Studies comparing extraction methods aiming to represent trace element concentrations in percolation water with more systematic experimental setups can be found elsewhere (e.g. Grathwohl and Susset 2009, Kalbe et al. 2007, Sahuquillo 2003 or Di Bonito 2005). Nevertheless, the experimental setup for the comparison conducted here was intended to imitate the situation in practical risk assessment. It allowed successful quantification of the uncertainty to be expected when conventional batch extracting methods were used to characterize in situ concentrations of trace elements.

5.2.3 Model structure

Pedotransfer functions based on Freundlich equations were only able to predict trace element concentrations with sufficient accuracy when sorption was the chief process for trace element retention. The tested pedotransfer functions are extended sorption isotherms based on the Freundlich equation, where a more general applicability of the sorption isotherms is realized by extending the Freundlich coefficient to include pH and other soil properties relevant for trace element retention. The investigations described in Chapter 4

showed that predictions on soils with $\text{pH} > 6.5$ displayed a rapid increase in model error. This phenomenon was especially visible for Ni predictions. With higher pH values, a variety of processes change the main retention mechanism of cationic elements in the soil (Harter and Naidu 2001). In the approach of extended sorption isotherms based on Freundlich equations, sorption is assumed to be the general retention mechanism for trace elements in the soil (Lewandowski et al. 1997). However, the log-linear model structure was not able to mirror the complex and interrelated mechanisms in near neutral and neutral pH milieus. Co-precipitation with carbonate enhanced retention of the trace elements, leading to a sudden increase in retention, which in turn resulted in underestimated solid phase concentrations of Ni and Cd (Chapter 4). On the other hand the solubility of organic carbon has been seen to be amplified in neutral pH milieus, increasing the solubility of trace elements which show an affinity for metal-organic complexation (Di Bonito 2005). Solid phase Cu concentrations have been overestimated in horizons with high pH-values and noteworthy C_{org} concentrations (Chapter 4). In deeper horizons with smaller C_{org} concentrations and higher pH values the opposite effects seemed to have cancelled each other out, leading to fairly accurate prediction of solid phase concentration of Cu with low model error. The multi-faceted interrelated retention mechanisms made PTF predictions very uncertain for soils with near neutral and neutral pH values. For proper model application it was thus not only important to observe the proposed range of validity. Additional or changing retention mechanisms can lead to a considerable degree of model error.

For concentrations of soluble trace elements lower than the range of validity PTF prediction was accurate to the same degree as predictions made for soils with trace element concentration within the range of validity. It has been reported that for low loading rates (< 0.6 mg/l) all Cd added was adsorbed independently of the pH value in smectite-dominated luvisol (Naidu et al. 1994, in Harter and Naidu 2001). This phenomenon should lead to underestimation of S_{PTF} concentrations when compared to $\text{Na}_2\text{-EDTA}$ extractable trace element concentrations. Underestimated concentrations were recorded for low concentration in the uncertainty analysis, but not for all elements. Since the underestimated concentrations occurred in parallel with increasing pH values, the experimental setup did not allow a certain source of model error to be distinguished. Model error due to low loading rates was as likely as the co-precipitation discussed above. Further studies with more elaborate experiment designs are needed to provide a more conclusive answer.

5.2.4 Model parameter

Relative to the concentration level, model error and uncertainty of the median were greater in subsoil horizons than in topsoil horizons, as was also recorded in the uncertainty analysis described in Chapter 4. One reason for the better prediction results in the topsoil may have been that trace element concentrations were higher, and thus uncertainty due to measurement error was lower. Another explanation may be that the physicochemical soil properties in the topsoil were closer to the centre of the training dataset. Since the PTF from Utermann et al. (2005) were parameterized semi-empirically by regression, the best fit will be at the centre of the data. The subsoil properties of the soils examined in Chapter 4 were mostly at the edge of the range of validity. A comparison of model accuracy in a variety of general purpose Freundlich sorption isotherms over wide concentration ranges showed that accuracy was usually lowest for low concentrations (Elzinga et al. 1999). Although not considered as an input parameter, the PTF predictions in Chapter 4 showed greater model error for soil with very low silt and clay content. The parameters of the model were thus not optimal for these kinds of soil materials. Specifically, CEC may not have been the best parameter for predicting potentially exchangeable solid phase concentrations in sandy soils with very low clay and silt content. CEC as an overall parameter for all the adsorption sites available (Lewandowski et al. 1997) showed the best fit for a large variety of soils which the training data set contained (Utermann et al. 2005). For soils with a low level of sorption, sites sorption capacity was probably more sensitive to parameters affecting the sorbate than the sorbent. Future studies will reveal which parameters these are in particular. Sandy soils usually have low sorption capacity toward trace elements (Freundlich coefficients for Cd $K_f < 1.5$), where the partition relationship between solid phase and soluble trace relation lay more in the liquid phase leading to low partition coefficients. In soils with small partition coefficients, variability in chemical properties has only minor influence on the variability of soluble trace element concentration; physical parameters such as the soil's dispersivity are more important, and Cd flux concentrations in the bottom of a soil profile mostly depended on deposition rate and soil-water distribution coefficient (Seuntjens et al. 2001). It may thus be necessary to examine the physicochemical mechanisms of trace element retention in soils with low sorption capacities more closely and exclusively in order to derive more suitable prediction models.

6 Conclusions

In risk assessment based on an analysis of trace element concentrations in percolation water, spatial variability was seen to be the predominant source of uncertainty. The spatial variability of Cd, Zn, Mo, Pb, Co and Ni was primarily correlated with the spatial variability of pH values. Thus the representativeness of background values for Cd, Zn, Mo, Pb, Co and Ni could be increased by grouping these according to pH values. The variability of As, Cu, V, Cr, Sb and Sn concentrations in percolation water was predominantly correlated with DOC concentrations. Therefore, the representativeness of the background values of As, Cu, V, Cr, Sb and Sn, could best be increased by grouping these according to DOC concentrations. In practical risk assessment, field scale spatial variability is of special concern. The absolute magnitude of spatial variability in the field scale of trace element concentrations in percolation water increased with rising concentration levels. In order to achieve comparable results, it thus proved best to quantify measures of uncertainty in relative terms, e.g. by using \log_{10} -transformed data. Inter-quartile distances in the field scale ranged in orders of magnitude from 0.22 to 0.42 within 90 m. Nonparametric confidence intervals showed a significant relationship with the concurrent inter-quartile distance. Due to the field scale spatial variability of soils and the resulting variability in trace element concentrations in the percolation water, statements concerning the exceedance or non-exceedance of threshold values could only be made with acceptable statistical uncertainty ($\alpha \leq 0.1$) when operational median concentrations were approx. 1/3 higher or lower than their critical insignificance threshold value.

When the current risk of groundwater contamination is assessed on the basis of concentrations in batch extracts, the concentration in the batch extract did not prove to reflect the in situ concentration with acceptable precision and accuracy. Due to the high level of imprecision of between 0.4 and 0.8, batch extracts could only be used to achieve a rough estimate of the current trace element concentration in percolation water. Results from batch extracts should thus always be clearly stated as what they are: the general leaching behaviour of the soil material under given experimental conditions. Adjustment of ionic strength to in situ conditions made it possible to increase the accuracy of estimations made with respect to cationic elements such as Cd, Co, Cr, Pb, Ni and Zn. Estimates of V or Mo were also more accurate in batch extracts with adjusted ionic strength, whereas in situ concentrations of As and Sb were estimated more accurately by aqueous batch extraction without adjustment of

the ionic strength. For most elements the precision of 5 l/kg extracts with adjusted ionic strength was only slightly better than the 2 l/kg extract without adjustment. However, given the general imprecision of both methods by orders of magnitude of between 0.4 and 0.8, it is questionable whether the slight improvement in precision and accuracy justifies the laborious protocol of 5 l/kg extraction with adjusted ionic strength.

When the future risk of groundwater contamination by trace elements is assessed on the basis of percolation water prognosis employing general purpose sorption isotherms founded on Freundlich isotherms (so called pedotransfer functions), uncertainty due to model error and uncertainty due to spatial variability are similar when sorption is the key mechanism of trace element retention. In these cases, pedotransfer functions based on Freundlich isotherms are a fairly reliable tool to estimate solid phase concentrations of Cr, Cu, Ni, Pb and Zn when uncertainty in the order of magnitude of up to 0.5 is acceptable. Application of pedotransfer functions to predict solid phase concentrations of Cr with model error in the order of magnitude of < 0.5 was only possible in topsoil horizons. Model error is the predominant source of uncertainty in soils with $\text{pH} > 6.5$, because in neutral and near neutral pH milieus co-precipitation and change of metal speciation cause an abrupt increase in trace element retention, which cannot be mirrored by the monotonic behavior of the general purpose pedotransfer function. The sensitivity analysis has shown that general-purpose pedotransfer functions based on Freundlich isotherms are more sensitive toward the invalidity of physicochemical soil properties than toward the invalidity of trace element concentrations in low concentrations.

Throughout the study, it became increasingly evident that the spatial variability of trace elements in percolation water was closely related to the spatial variability of physicochemical properties in the soil. In contrast to the effects of regional scale spatial variability on the uncertainty of central estimates, which can be reduced to some extent by stratification, the uncertainty which field scale spatial variability imposes on statistical estimates of the central tendency can only be reduced by increasing the sample size. Future research should thus focus on methods to facilitate a quick preliminary overview of the spatial variability of physicochemical properties. Knowledge of the field scale variability of sorption-relevant physicochemical properties will allow the researcher to identify appropriate sample sizes; this is crucial in order to reach a balance between the economic feasibility and scientific precision of risk assessment for trace elements in the soil groundwater pathway.

7 References

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8 Annex

Erklärung zur Dissertation

Hierdurch erkläre ich, dass die Dissertation "Sources of uncertainty in precautionary risk assessment of mobile and potentially mobile trace elements in the soil groundwater pathway " selbständig verfasst und alle benutzten Hilfsmittel sowie evtl. zur Hilfeleistung herangezogene Institutionen vollständig angegeben wurden.

Die Dissertation wurde nicht schon als Diplom- oder ähnliche Prüfungsarbeit verwendet.

Hannover, den 17.10.2012

Levke Poppe Godbersen

Curriculum Vitae

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Geboren als Tochter von Sigrun G. Godbersen geb. Schmelzer und Dr. Godber W. Godbersen am 21.07.1980 in Eutin.

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- 1990 – 1999 Internat Stiftung Louisenlund, Allgemeine Hochschulreife
- 1996 – 1997 Sedbergh School, Canada (Schüleraustauschprogramm)
- 1999 – 2000 Universität zu Köln, Regionalwissenschaften China
- 2000 – 2007 Humboldt Universität, Berlin, Diplom Geographie. Diplomarbeit: „Variationsbreite und ökologischer Zustand der Böden des Berliner Flughafens Tempelhof“ Inventur und Kartierung der Böden des Flughafens im Maßstab 1:10 000 zur weiteren Verwendung im FIS-Broker der Senatsverwaltung für Stadtentwicklung Berlin
- 2007 – 2008 Bundesanstalt für Geowissenschaften und Rohstoffe. Wissenschaftliche Angestellte im Arbeitsbereich “Wasser- und Stoffhaushalt im Boden“
- 2008 – 2010 Leibniz Universität, Hannover, Institute für Physische Geographie und Landschaftsökologie, Wissenschaftliche Angestellte
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Publications

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