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Scaling of Sorption Isotherms to Quantify the Field-Scale Variability of Heavy Metal Retardation in Soil

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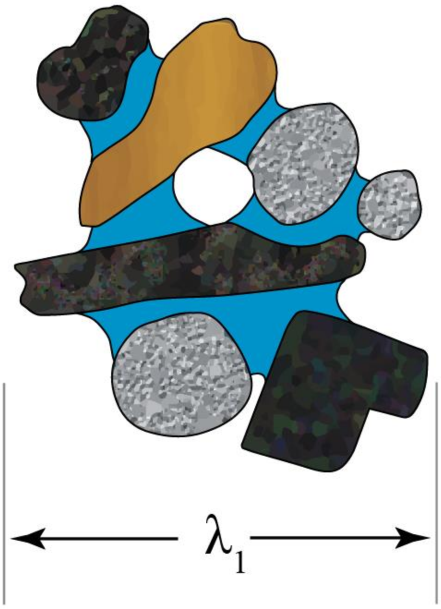

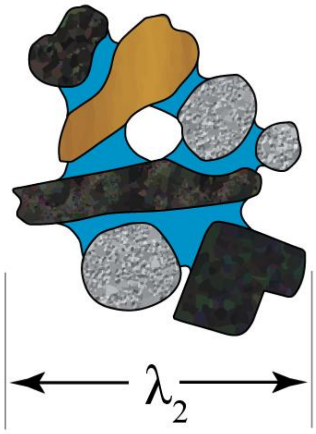

Scaling of Sorption Isotherms to Quantify the Field-Scale Variability of Heavy Metal Retardation in Soil

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Abstract

Keywords: heavy metal sorption, scaling, field-scale variability

Taken two agricultural lands as the study areas (loess, Haplic Luvisols; loamy to sandy soil, Eutric Cambisols), which are representative of the soils of northern Germany, this dissertation studies the upscaling of the adsorptive binding of heavy metals in soils and their variability by calculating the scale factors. The adsorptive binding of heavy metals in soils is mostly quantified by sorption isotherms with large variability at the field scale. The aim of this work is to search the correlation of sorption isotherms by means of scale factors between different heavy metals and further with physico-chemical soil properties, so that only a few measurements are necessary to make sufficient statements on heavy metal's binding and mobility at field-scale. At both study sites, upscaling can capture the linear parts of sorption's variability well. Scenario study discussed satisfied simulations of heavy metals transport process, where the scale factors are treated as the measure of variability. However, in the statistical and geostatistical studies, no significant correlations were found between the scale factors of different heavy metals and with physicochemical soil properties. Depending on the location and soil horizon, the correlation of scale factors between different heavy metals varied so different and not transferrable. In addition, the reference isotherm calculated directly from measurements did not match the sorption isotherm from a composite sample, which indicates that scaling is favorable to homogenous sites. Thus, the important finding in this dissertation can be summarized that the application of scale factors for heavy metal sorption isotherms, such as statistical or geostatistical evaluation, is limited only to specific case studies or a scenario modeling.

Kurzfassung

Schlüsselwörter: Schwermetallsorption, Skalierung, feldskalige Variabilität

Wurden zwei Ackerlande (Löss, Parabraunerde; Geschiebedecksand, Braunerde) als die Untersuchungsstandorte genommen, die für die Böden des Norddeutschlands repräsentativ sind, diese Dissertation studiert Upscaling der adsorptiven Bindung der Schwermetalle in Böden und deren Variabilität durch der Berechnung von Skalierungsfaktoren. Die adsorptive Bindung der Schwermetalle in Böden wird meist mit Sorptionsisothermen quantifiziert und die weisen feldskalige große Variabilität auf. Ziel dieser Arbeit ist es, die Korrelation der Sorptionsisothermen mittels Skalierungsfaktoren zwischen verschiedener Schwermetalle und weiterhin mit physikochemischen Bodeneigenschaften zu suchen, damit nur wenige Messungen erforderlich sind, um feldskalige Aussagen zur Schwermetallbindung und Mobilität machen zu können. An beiden Untersuchungsstandorten, Upscaling können der linear Variabilitätsanteil der Sorption gut erfassen. Szenarium Studie befasst sich mit guten Simulationen des Schwermetalle Transportprozess, wobei die Skalierungsfaktoren als der Maß der Variabilität sind. Allerdings, in den statistischen und geostatistischen Studien waren keine signifikanten Korrelationen zwischen den Skalierungsfaktoren sowohl verschiedener Schwermetalle als auch mit physikochemischen Bodeneigenschaften gefunden. Je nach Standort und Bodenhorizont variiert die Korrelation der Skalierungsfaktoren zwischen verschiedenen Schwermetallen so unterschiedlich und nicht übertragbar. Auch die Referenzisotherme aus direkte Messungen passen nicht mit der von einer Mischprobe resultierte Sorptionsisotherm, dass Skalierung geeignet für die homogenen Orte ist. Somit lasst sich der wichtige Befund in dieser Dissertation zusammenfassen, dass die Anwendung von Skalierungsfaktoren für Schwermetallsorptionsisothermen wie beispielsweise auf statistische oder geostatistische Auswertung nur für konkrete Fallstudien oder für eine Modellierung der Szenarien eingeschränkt ist.

Chapter 1 Introduction

1.1 Purpose and meaning of this study

Soils are the most alive parts on the surface of the Earth and the soil science or pedologie is the study of soil as a natural resource by exploring the function, development as well as their distribution (Scheffer and Schachtschabel, 2010). Various kinds of pedological problems, e.g. soil processes with cycles of water, carbon, and nutrients and soil/environmental contamination, must be considered and evaluated at higher scale hierarchies of catena, soil region, landscape and so on (Pachepsky and Hill, 2017). The retardation of reactive substances in soil is one of these problems, despite investigative effort and deeper understanding of process knowledge last decades. On the one hand, the soil scientists usually have data collected at measurement or small scale. On the other hand, the farmers, who fertilize the farmland, or the policy makers, who take decisions of threshold values, need to know the results of environmental diagnostics, monitoring, and predictions at much larger scales. And yet, understanding of reactive substance’s behavior in soil at the scale of measurement do not always lead to a better description of processes at the scale of application (Deurer and Böttcher, 2007). Scaling, as the generally used scientific term, is the transfer of information between hierarchy levels or scales and is treated as a great challenge to connect the behavior and characterization between small scale and field scale and to evaluate their validation and efficiency by the corresponding models (Blöschl and Sivapalan, 1995). It is widely recognized that the scaling is not easy and the reasons that scaling usually fails are many, e.g. unknowable conceptual model errors, discrepancy in the scale of model occuring over a multitude of spatial and temporal scales, uncertainties related to model choice and omnipresent chemical and physical heterogeneities (Miller *et al.*, 2010; Vereecken *et al.*, 2016).

The purpose of this study is to investigate the field-scale variability of reactive substances retardation in soil on sorption isotherms and a variety of physico- chemical soil properties by applying Miller's scaling technique to overcome problems of heterogeneity. In this dissertation, two study sites are selected, targeting soil samples along a transect retrieved from Haplic Luvisols near Lathwehren and Eutric Cambisols at Vinnhorst in the region of Hannover, Germany (Fig. 1.1). The primary aim is to quantify the relationship between the scaled sorption isotherms of heavy metals and the attendant physico- chemical soil properties by the means of statistical and geostatistical methodes. In addition, a numerical modeling of the heavy metal transport in unsaturated soils with upscaling the sorption process was simulated. In the following part of this chapter, the basic mechanism of heavy metals in soil, the physico-chemical soil properties impacting sorption and the history of Miller-Miller scaling theory were briefly reviewed. Three scientific questions and associated objectives were subsequently listed. Finally jet importantly, the outline of this dissertation was highlighted.

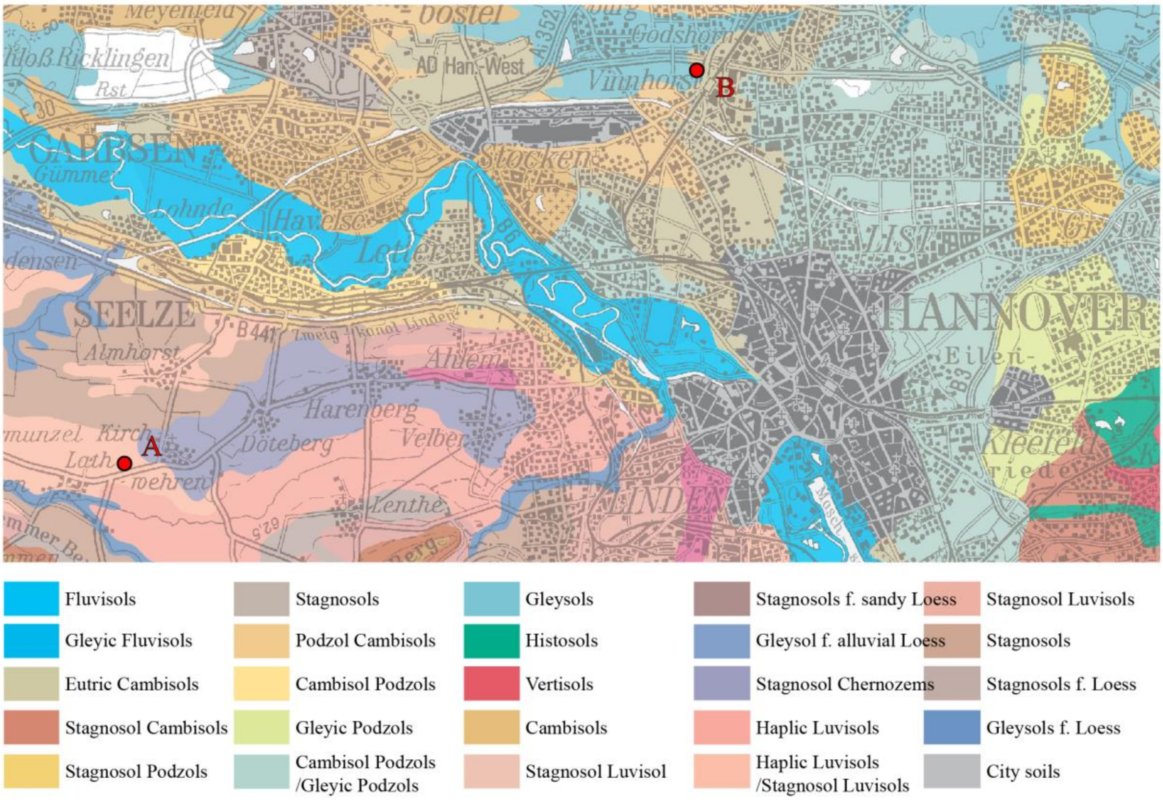

Figure 1. 1 Overview soil map with different soil types and showing the localities of the two study areas (source: http://www.bgr.bund.de). A: the sampling site in Lathwehren. B: the sampling site in Vinnhorst

1.2 Research progress in Germany and abroad

1.2.1 Heavy metals in soils

The term “heavy metal” refers to the group of metals and metalloids of relatively high atomic mass (>5 g/cm^3) (Alloway, 2012). In soil chemistry, heavy metals are grouped into trace element, where differ from other ‘major’ element constituting over 99% of the total element in world soil, including oxygen, silicon, aluminium, iron, calcium, sodium, potassium, magnesium, phosphorus, and so on (Sposito, 2008). Although trace elements are minor components of the solid phase of the earth’s crust, heavy metals and metalloids play an crucial role with biological effects. In trace amounts, most of these elements, like copper, zinc and cobalt, are beneficial to biosphere, the natural environment of living organisms. However, when their concentrations in the environment or in organisms are too high (extending the threshold value), they become detrimental. Even at very low ambient concentrations, some elements unknown with any essential biochemical functions, like mercury and lead, have the potential to injure the living organisms(Violante *et al.*, 2012).

Anthropic impact on the biosphere is a critically important factor, which influence the environment very broad and complex; and somw times irreversible (Kabata-Pendias, 2011). Anthropogenic sources are including irrigation water, atmospheric deposition, land application of agricultural materials, sewage sludge, as well as industrial wastes (Naidu et al, 1997). Relating to the heavy metals, atmospheric deposition is the most extensive form of contamination (Alloway, 2012). The air pollution has arisen from almost every combustion process and in many industrial sources in the form of dust and gaseous emissions (Bradl, 2005). For example in Germany, the emission of copper and zinc in 2015 increased by approximately 30.7% and 20.9%, respectively, compared to 1990 (UBA, 2017). The Protocol on Heavy Metals, an extending protocol to the Convention on Long-Range Transboundary Air Pollution, was approved in Denmark by the United Nations Economic Commission for Europe in 1998 to gradually reduce cadmium, lead and mercury emissions (Sands and Peel, 2012).

The atmospheric deposited heavy metals and accompanying metalloids on the Earth's surface (mostly the bare soils) can be retarded and involved in a series of complex physical, chemical and biological interactions, including sorption–desorption reactions, precipitation and dissolution, oxidation–reduction, and solution and surface phase complexation (Violante *et al.*, 2007). The most significant process of heavy metal retardation in soil is the strong adsorption by the organic, and inorganic, colloidal constituents of soil, which controls the mobility and leaching danger in soils (Travis and Etnier, 1981).

Soil scientists use different models to quantify heavy metals and metalloid ion adsorption by soil components, which are divided into two most common model groups, namely empirical adsorption models and chemical surface complexation models. A discussion on chemical surface complexation models is beyond the scope of this chapter, but can be found in the paper by Goldberg and Criscenti (2007). The empirical adsorption models has long history in soil chemisty, where as showed in their names, the description of experimental adsorption is realized through an isotherm. The sorption isotherm is a relationship bewteen the concentration of a solute on the surface of an adsorbent and the concentration of this solute in the liquid phase, where the temperature maintains (Scheffer and Schachtschabel, 2010). Linear sorption isotherm is the simplest form and widely used at a lower concentration. As nonlinear isotherm, Freudlich and Langmuir sorption isotherms are mostly discussed in soil science (Selim, 2015). Althought the non-linear function is more appropriate for describing the heavy metal’s sorption in soil, the quantification of their field-scale variations becomes difficult. A thorough discussion to solving the functional relations by scaling methodes is given in *Chapter 3*.

1.2.2 Impact factor of sorption: physico- chemical soil properties

As stated in the last Section 1.2.1 the heavy metals and metalloids in soils are involved in a series of complex physical, chemical and biological processes, which in turn are related with several physico- chemical soil properties. A systematic discussion for understanding the fate on their relationship with soil properties was proposed by Buchter *et al.* in 1989, where they compared the correlation between Freundlich parameters K_d and n of 15 elements, also including heavy metals, and soil properties by 11 American soils (Buchter *et al.*, 1989). They found that the most important soil property affecting sorption is pH; and cation exchange capacity influences the K_d value, when the initial speciation of elements is cation.

Concurrently in Europe, some Dutch soil scientists investigated the sorption behavior with soil properties by modeling the transport of reactive solute in spatially variable soil systems, where they derived a sorption equilibrium model of cadmium that K_d was tightly correlated with pH and organic matter content (Van der Zee and Van Riemsdijk, 1987; Boekhold and Van der Zee, 1992a). Boekhold and Van der Zee (1992b) named this relation as a “scaled sorption model”. Actually, this modification of sorption equilibrium model is in the same spirit as pedotransfer functions, which use statistical regression equations to express relationships between soil properties, and have been developed mainly in soil hydrology to predict soil water retention and hydraulic conductivity curves (Wösten *et al.*, 2001).

Thereafter, the prediction of solute adsorption parameters from basic soil properties by the means of pedotransfer functions has gained more attention in Germany. Springob and Böttcher (1998) parameterized the Freundlich coefficient of cadmium sorption in a sandy soil with three soil properties, namely organic carbon content, clay content and pH. Streck and Richter (1997) took the same strategy as Boekhold and Van der Zee (1992b) to model the cadmium and zinc displacement in a sandy soil at the field scale. Horn *et al.* (2004) also developed a pedotransfer function of cadmium sorption by using even more soil properties and found high goodness-of-fit for the approaches.

In the 21st century, the increasing applications of fertilizers, and agricultural and industrial wastes to soils is also taken very seriously by environmental scientists. Sauvé *et al.* (2000) compiled data from more than 70 studies collected from the literature and summarized that the best correlated physico- chemical soil properties are pH and organic matter content. Carrillo-González *et al.* (2006) reviewed the impact factors including soil pH, chemical speciation, soil organic matter, fertilizers, redox potential, clay content and soil structure. Loganathan *et al.* (2012) complemented that cadmium sorption in soils is influenced as well by the kinetics of sorption.

1.2.3 Miller-Miller scaling theory

In 1956 the theory of similitude and the attendant technique named “scaling” was firstly proposed by two brothers Edward Miller and Robert Miller in soil physics (Miller and Miller, 1956). The concept of scaling theory or similitude analysis has long been used in applied physics to analyze the relationships between physical functions with the minimal number of variables, by casting the variables into dimensionless form. At that time, this concept seemed to be obvious and logical, since the soil scientists could hardly generalize quantitative physical theories owning to the extreme variability of our soils. The Millers tried to make it more accessible to soil science and defined the appropriate criteria in soil hydrology research with two geometrically similar media that differs only by a characteristic length. Figure 1.2 illustrates such “similar media” that can be scaled with mutually exchangeable characteristic length (e.g., λ_1 and λ_2). A detailed scaling method based on the Miller-Miller similar media theory is given in *Chapter 3*.

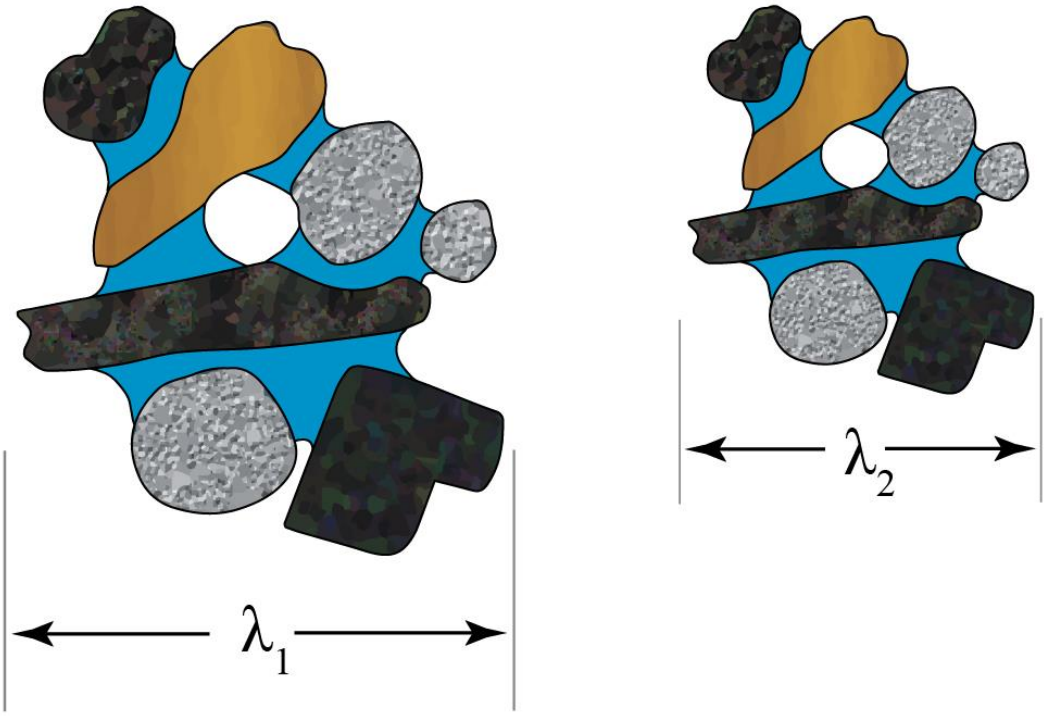

Figure 1. 2 Schema of two “similar media” in a geometrically “similar” partical systems. λ_1 and λ_2 are the characteristic lengths. Modified after Böttcher (1997).

Indeed, no plausible methode has been existed to explore a geometric similarity microscopically in 1950s and such “detailed similarity throughout the microscopic geometries of two media” by Millers’ statement “has zero probability”. Hence, the researchers among the first studied soil properties into the physical behavior of soil-water systems with coarse materials in the range of sands. For example, Klute and Wilkinson (1958 and Wilkinson and Klute, 1959) practiced firstly by soil-water retention curves coalesced into a single-scale mean function with graded sand and Elrick *et al.* (1959) tested capillary flow by evaluate the scaling in similar sands.

As the result had no guarantee for maintaining similarity in media (eg. in pore space) and was limited by the sandy soil, the attention of soil scientists was turned into the infilteration by the classic work of Philip (1955, 1957) at the same period. Until 1970s the Miller-Miller similar media theory was picked up afresh as a promising approach for the field studies of soil-water behavior against natural heterogeneity in field soils. A series of studies took the idea from Miller and Miller's original concept using regression techniques rather than dimensional analysis to obtain the so called scale factors for soil water properties (Reichardt *et al.*, 1975; Warrick *et al.*, 1977; Simmons *et al.*, 1979).

The scale factors calculated from the scaling procedure could reduce the hydraulic properties of various sampling locations to an average relationship; at the same time maintain the variability for every single scale factor. Comparing to the original concept two further assumptions was made, where 1) the using of saturation degrees instead of volumetric water content didn't need to assume similar media to exhibit identical porosities and 2) the regression by the minimizing the sum of square to one avioded a search of microscopic physical length. This regression-based scaling method was named by Tillotson and Nielsen (1984) as "functional normalization".

Subsequently, Miller's scaling gained its popularity in soil hydrologie and was widely used as a convenient method to identify the spatial variability of soil hydraulic properties (Jury *et al.*, 1987; Vogel *et al.*, 1991; Ahuja and Williams, 1991; Kosugi and Hopmans, 1998; Ursino *et al.*, 2000; Das *et al.*, 2005; Vogel *et al.*, 2010; Schlüter *et al.*, 2012; Sadeghi *et al.*, 2016). Integration of Miller's scaling at solving other soil physical problems was motivated. Spaans and Baker (1996) attempted to measure soil freezing characteristic and simulate the transport of water, heat, and solutes numerically in a two-dimensional Miller-Miller similar media. Selker and Schroth (1998) used the sorptivity by contact angle to examine the validity of scaling of macroscopic dimensions. Schwen *et al.* (2015) investigated the spatial and temporal variability of soil gas diffusivity by the means of scaling.

1.3 Tasks of this study and dissertation outline

1.3.1 Research questions and objectives

Understanding the retardation of reactive substances in soil is a crucial step for modeling the fate of many environmental chemicals. This process can be strongly influenced by the variability in the biogeochemical conditions over the spatial domain. The study how to quantify this spatial consideration is still infancy due to the lack of appropriate methods. First, direct determining sorption *in situ* is impossible. Second, the adsorption experiments, which can be performed in either a closed system (batch reactor) or an open system (flow-through column), are both expensive and time consuming (Sposito, 2008). Other modern methods, i.e. spectroscopic and microscopic tools, did provide a new way to interpret the sorption processes and mechanisms on the solid structure microscopically. However, soils are such complicated mixtures of mineral and organic compounds that the adsorption experiments determining sorption isotherm will be used for a long time (Limousin *et al.*, 2007). Some soil scientists develope statistical methods to indirectly estimate isotherm parameters of heavy metals, e.g. artificial neural networks (Anagu *et al.*, 2009), tree regression analyses (Vega *et al.* 2010) and bayesian approach (Anagu *et al.*, 2012). These methods are sophisticated and practical, however, a vast amount of sorption data is still needed, which are mainly derived from adsorption experiments.

For the first time, Böttcher (1997) employed Miller-Miller scaling theory to scale cadmium sorption isotherms in soils. It was demonstrated that the scale factors calculating from the scaling procedure could reduce the sorption isotherms to an average relationship, while the variabilities are also maintained for every single scale factor. In a subsequent study (Böttcher, 1998), a significant correlation between the scale factors of sorption isotherms of cadmium and zinc, measured by adsorption from single-metal solutions, was found. However, because these works were limited to a sandy soil and two heavy metals, further experimental investigation is needed.

The first objective of this dissertation was composed of two correlations, where the one was to test the relationship of the scale factors of sorption isotherms between the different, mostly competitively sorbed heavy metals (cadmium, copper, lead, and zinc) and another one was the comparison of the relationship between the calculated scale factors from the sorption isotherms of the heavy metals and the corresponding physical (clay content), chemical (pH, CEC, and oxides) and biological (organic carbon) soil properties.

The second objective was to confirm, if the average relationship of isotherms can be represented with one single measured isotherm in a composite sample from the whole investigation area. As a possible result, a sufficiently certain quantification of the field-scale variation of heavy metal retention and mobility in soil may be obtainable from a combination of only a few of the expensive and time consuming measurements of heavy metal sorption, extensive measurements of soil properties, and calculation of scale factors of sorption isotherms from soil properties using multiple regression.

The third objective was to model different scenarios of heavy metal transport in unsaturated soil. Spatial variability of sorption at every sampling point was represented using a scale factor, which was either directly calculated (using a scaling procedure) or indirectly estimated (using regression models with another heavy metal or from soil properties). The performance of the two scaling procedures in simulating spatially variable heavy metal transport should be compared to simulations with original sorption data, where the results would extend the use of scale factors from statistical description of spatially variable sorption isotherms (direct scaling procedure) to broadened application in prediction of reactive transport processes in soil by the indirect scaling procedure.

1.3.2 Outline of the dissertation

This dissertation is divided into six chapters, which includes the Introduction (*Chapter 1*) and Final discussion (*Chapter 6*). The main part constitutes a compilation of three manuscripts which have been published in or are preparing for submission to international scientific peer-reviewed journals. Repetitions are inevitable in some places (e.g. methods) of each manuscript. The three manuscripts are assigned into four chapters (*Chapter 2, 3, 4 and 5*). The brief overview of each study is listed as below.

In *Chapter 2*, the measurement and sampling are briefly discussed. The sampling strategy was to collect samples along a transect, which is able to describe the entire field-scale variability of sampling sites, and makes different methods for evaluation of spatial variability (geostatistics, spectral variance analysis) applicable.

Chapter 3 consists of one manuscript that scaling was applied to simplify the description of the statistical variations in the sorption properties at the field scale. a statistical analysis of the correlation between the scale factors of different heavy metals, and between scale factors of heavy metals and basic soil properties and the uncertainty of scaling, which occurs during the quantification of the variability of sorption isotherms from measurements, scaling procedures and site-specific variations is presented.

Chapter 4 investigates the field-scale variability of heavy metal sorption in soil by the means of scaling and explored the hierarchical structure and nonstationarity of scaled sorption behaviour in space with other physico-chemical properties by multivariate statistics and geostatistics. The spatial structural relationships between scale factors of heavy metal sorption and soil properties were analysed with a linear model of coregionalization and principal component analysis according to the potential correlations at different scales. In one study region, nonstationary in the mean was observed and the data were transformed by residual maximum likelihood.

Chapter 5 simulates the heavy metal transport with HYDRUS model using a unique reference sorption isotherm (derived using the scale procedure or mixed soil samples), where the spatial variability of sorption was accounted by direct calculation of scale factors for sorptions or indirect calculation of scale factors from physicochemical soil properties. And for comparison, variability of sorption was also simulated using the original measured Freundlich parameters.

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Chapter 2 Measurement and Sampling Summary

2.1 Survey of study area

2.1.1 Sampling site and strategy of sampling

In this study, two sampling sites (permanent agricultural land) in the region of Hannover, Germany, were selected: one with loess-derived Haplic Luvisols, located near Lathwehren (LA), and another with Eutric Cambisols from loamy to sandy deposits, located near Vinnhorst (VI). The sampling strategy was to collect samples along a diagonal line (transect) of the total area (approximately 1 hectare). This method is considered because transect sampling is able to describe the entire field-scale variability of sampling sites (Cassel *et al.*, 2000), and makes different methods for evaluation of spatial variability (geostatistics, spectral variance analysis) applicable (Nielsen and Wendroth, 2003, Pennock *et al.*, 2008). Each sampling site was divided into two horizons (topsoil: 0 - 30 cm, subsoil: 30 - 60 cm). For each horizon, 50 samples were taken along a transect at 5-m intervals; thus, in total, 200 soil samples were collected from the four horizons. Each sample consisted of four auger subsamples taken in the close vicinity around the particular location. The four subsamples were mixed and bulked. All soil samples were air dried and sieved to remove particles larger than 2 mm. The material < 2 mm in grain size was used for the analyses. In addition, for each horizon, we took 5 g of material from each of the 50 samples and homogenized these into a single, composite sample.

2.1.2 Laboratory measurement

The 204 prepared (200 natural samples and four composite samples) soil samples were analyzed in the laboratory of the Soil Science Institute of Hanover. Several basic soil physico-chemical properties were measured (Table 2.1).

Table 2. 1 Methods for measuring physico-chemical soil properties. (Source: Utermann *et al.*, 2005)

Soil property [Unit]	Method
Texture [%]	Pipette method after Koehn (<63 µm)
	Dry sieving (>63 µm)
	DIN* 19683-2
pH ($CaCl_2$) [-]	Potentiometric by use of a glass electrode in 0.001 M $CaCl_2$
	DIN ISO^ 10390:1997
Total carbon [%]	C-N-S elementary analysis
	DIN ISO 10694
Total carbonate [%]	Gas volumetric
	DIN ISO 10693 (1997)
Total organic carbon (OC) [%]	Difference between total carbon and total carbonate
Oxalate extractable oxide by Fe, Mn and Al	Extraction with oxalic acid ammonium oxalate DIN 19684-6
(Fe_{ox}, Mn_{ox}, Al_{ox}) [mg kg^{-1}]	Measure with flame-AAS
Effective cation exchange capacity	Percolation with 0.1 M $BaCl_2$
(CEC_{eff}) [$mmol_c$ kg^{-1}]	Modified by DIN 19684-8
	Measurement of Ca, Mg, K, Na, Fe, Mn and Al with ICP-OES, determination of H^+ ion concentrations from pH value

* German Institute for Standardization

^ International Organization for Standardization

For determination of the sorption isotherms, 7 g of each sample was added to a $Ca(NO_3)_2$ electrolyte solution with different concentrations according to different standards (Heidkamp, 2005). Cd was then added as $Cd(NO_3)_2*4H_2O$ at a Cd concentration of 0.5 to 20 mg/l, Cu as $Cu(NO_3)_2*3H_2O$ at a Cu concentration of 1 to 40 mg/l, Pb as $Pb(NO_3)_2$ at a Pb concentration of 2 to 100 mg/l and Zn as $Zn(NO_3)_2*6H_2O$ at a Zn concentration of 2 to 80 mg/l. The soil-solution ratio was 1:5. The soil suspension was rotationally shaken for 24 h at 20 ℃. After centrifugation (15 min at 3600 g), the residual concentration of heavy metal in the supernatant was measured after each other by inductively coupled plasma optical emission spectrometry (ICP-OES) and, if necessary, by inductively coupled plasma mass spectrometry (ICP-MS) after dilution. The initial content of the adsorbed heavy metals of each sample was derived via extraction with a solution of Na_2-EDTA (soil-solution ratio was 1:10).

2.2 Varity of sorption isotherm and soil parameters

2.2.1 Choosing models

The adsorbed amount, S, was calculated from the difference between the initial added concentration, C_i, and residual concentration, C, in the supernatant with simultaneous consideration of the native adsorbed amount, S_0, and the term m refers to the soil:solution ratio:

$$S = m(C_i - C) + S_0. \tag{2.1}$$

The adsorbed term S in Equation (2.1) and the residual concentration C usually have a nonlinear relationship, which was described by the Freundlich equation:

$$S = KC^n, \tag{2.2}$$

where K is the Freundlich coefficient and n is the Freundlich exponent.

The Freundlich equation can be transformed to a linear form:

$$\log S = \log K + nlogC. \tag{2.3}$$

Hence, $log\ K$ is the intercept, and n is the slope when Equation (2.3) is graphically expressed. A disadvantage of the linear form is the insensitivity (Goldberg, 2005). Thus, the fitting of the sorption isotherm was performed with a quality control, which was applied by using the methods from Utermann *et al.*, (2005).

2.2.2 Characterization of the soil properties and the sorption isotherm

The essential requirement for the comparison of the correlation by means of statistics is the distribution of the sorption isotherms and the sorption-relevant soil properties within the sample collection. Table 2.2 lists the basic statistical information of the soil properties, including pH, effective cation-exchange capacity (CEC), and texture, which contains only the means and coefficients of variation (mean divided by standard deviation). The raw data provides an overview of the four soil horizons. In Lathwehren, the soil pH was near neutral in the topsoil and slightly alkaline in the subsoil. For Vinnhorst, the pH was slightly acidic and decreases from the topsoil to subsoil. The texture at each site did not change between topsoil and subsoil. Clay is considered to be the most influential factor for sorption. Clay represented approximately 12% of the soil at LA and approximately 17% at Vinnhorst. The sand content was small for Lathwehren but dominated the texture at Vinnhorst. The organic carbon content was considerably higher for Vinnhorst and decreased from the topsoil to the subsoil. In general, the variability of the soil properties at Vinnhorst was much larger than at LA, especially for the Vinnhorst subsoil.

Table 2. 2 Summary statistics of soil properties. A: At Lathwehren. B: At Vinnhorst.

A		pH	CEC_{eff}	OC	Carbonate	sand	clay	silt	Fe_{ox}	Al_{ox}	Mn_{ox}
		-	$mmol_c kg^{-1}$	-------------------mass%--------------------					--------- gkg^{-1}--------		
Mean	Topsoil	6.9	101.3	1.3	0.0391	3.8	11.1	85	2.6	0.6	0.3
	Subsoil	7.2	73.7	0.3	0.0395	3.3	12	84.9	2.6	0.6	0.2
CV [%]	Topsoil	2.2	9.8	36.7	113.1	11.5	8.7	1.2	3.7	3.7	10.9
	Subsoil	1.9	16.5	40.2	127.2	10.0	12.9	1.7	5.1	6.3	16.4
B											
Mean	Topsoil	5.9	145. 6	3.5	0	48.7	17.2	34.1	4.5	1.3	0.2
	Subsoil	5.3	197.1	0.6	0	44.7	17.6	37.7	5.8	0.4	0.2
CV [%]	Topsoil	7.5	18.4	20.5	0	18.5	23.3	15.1	22.2	26	30.7
	Subsoil	18.9	12.9	45.9	0	36.7	38	29.2	69.3	46.7	132.8

The physical soil properties are represented by the texture data. In the scaling theory, the fundamental point of sorption similarity was also based on the geometric similarity of soil particles. We assumed that the sorption isotherm must be correlated with the microscopic structure of the soil. Clay has often been found to have a great affinity for dissolved heavy metal ions (e.g., Springob and Böttcher, 1998b, Vega *et al.*, 2010). Figure 2.1 shows a texture triangle with all the soil sampling points of the four sampled horizons. It provides not only the texture information for soil classification but also the variability of the sites. As shown in Figure 2.1,

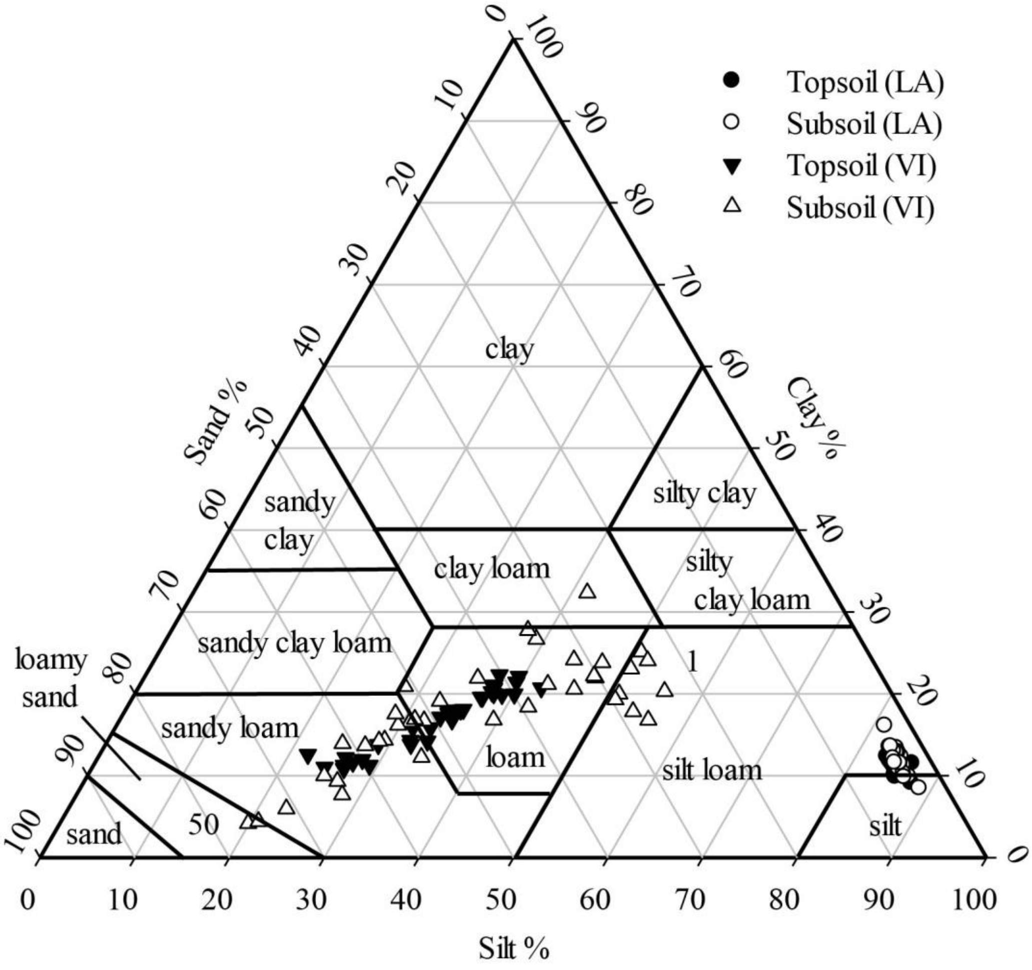

Figure 2. 1 Texture triangle with texture data of the soils at the sampling sites Lathwehren and Vinnhorst according to the world reference base (IUSS Working Group WRB, 2014).

the main texture of both horizons at Lathwehren was silt with only slight variation. In contrast, the texture of the Vinnhorst site was not as homogeneous and included a broad range from loam to sandy loam. In particular, the subsoil horizon extended across at least three texture classes. According to the sampling numbers 1 and 50, which were marked in Figure 2.1, the data showed that although the texture was highly variable, it could still be treated as spatially continuous.

The parameters K and n are representative values of the sorption isotherm, and their statistical means and coefficients of variation are shown in Table 2.3. All data sets could be parameterized by the Freundlich Equation, indicating that sorption is the predominant retardation process at the given concentration level. The parameter K varied much stronger than n, which has been confirmed by many other studies as well (e.g., Springob and Böttcher, 1998a; Deurer and Böttcher, 2007; Altfelder *et al.*, 2007). Considering the CVs of n in the Vinnhorst subsoil in Table 3B, the variation of n was still relatively strong.

2.2.3 Relations between Freundlich parameters

The most common methods of correlation analysis are Pearson’s correlation and Spearman’s rank correlation. In a study by Deurer and Böttcher (2007), the Spearman’s method was performed, but this method might be inappropriate for our objective because the actual values are replaced by their ranks and it would not exhibit the real but the distributional relationships (Douaik *et al.*, 2011). Therefore, Pearson’s correlation was used in this study. According to the classical statistical theory, the data needs to satisfy five conditions (Warner, 2008). First, each variable must be independent. Second, the variables should be quantitative and normally distributed. Third, between the two variables, the linear relationship must be followed, and the

Table 2. 3 Summary statistics of sorption isotherm parameters K and n. A: At Lathwehren. B: At Vinnhorst.

A		Cd		Cu		Pb		Zn	
		K*	n	K	n	K	n	K	n
Mean	Topsoil	1407.4	0.81	250.3	1.34	74815	0.66	7497.7	0.51
	Subsoil	2271.2	0.8	148.2	1.62	87415	0.66	13509	0.49
CV [%]	Topsoil	34	6.6	38.4	8.3	29.2	21	24.2	5.1
	Subsoil	32.7	5.9	59.2	10.2	28.9	18	17.3	6.6
B									
Mean	Topsoil	967.3	0.8	558.2	1.08	22549	0.74	1995.6	0.65
	Subsoil	719.3	0.95	1082.8	0.95	48817	0.68	3031.9	0.7
CV [%]	Topsoil	44.8	10.9	32.9	7	58	9.1	71.8	11.9
	Subsoil	134.3	8.8	96	40.2	109.3	17.7	134.3	21.7

*The unit of K is $\mu g^{1-n}L^{n}$ and the unit of n is unit less

bivariate normal distribution is also required as the fourth condition. The last condition is that the two variables should have roughly equal or homogeneous variance.

When we compared the coefficients of variation of these two parameters for all heavy metals and all sites, the result exhibited a linear relationship with rather weak correlation (regression all data in Figure 2.2, $r = 0.44$). Four of the data points were located far from the regression line, outside the 95% confidence band (Figure 2.2). On trial, we assumed these data to be outliers, and calculated a second regression (regression without outliers in Figure 2.2, $r = 0.97$). The regression line is more or less the same, and the close correlation indicates that the variability of n was mostly not independent of the variability of K. This finding could improve studies of pedotransfer functions of heavy metal sorption in soil, where n is usually neglected while indirectly deriving *K* from soil properties (Streck and Richter, 1997). Buchter *et al.* (1989), who did not directly compare the CVs of *K* and *n*, concluded from a comprehensive data set of sorption that *K* and *n* are both correlated with pH, which might support our findings from other perspectives. However, the four outliers indicate that some uncertainty with the interpretation of the variability of Freundlich *K* and *n* remains.

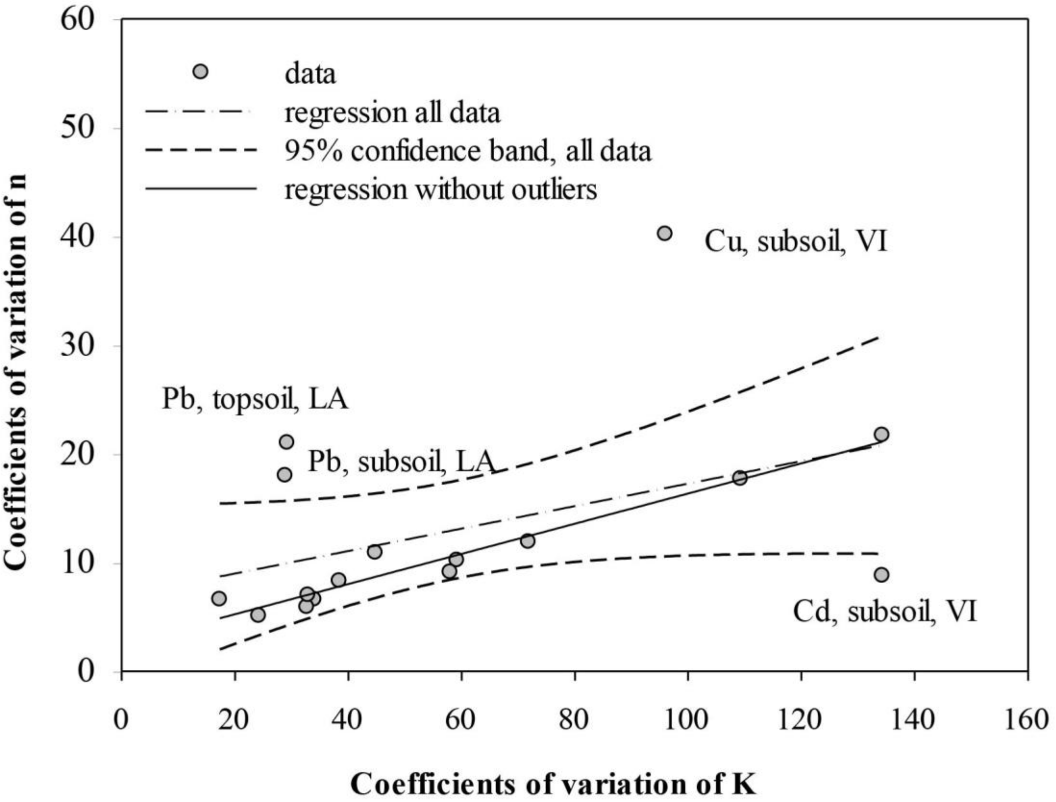

Figure 2. 2 Relation between Freundlich parameters *K* and *n* (expressed by the coefficients of variation, CV).

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Chapter 3 Scaling of Sorption Isotherm and Soil Properties

3.1 Evaluation of Field-scale Variability of Heavy Metal Sorption in Soils by Scale Factors – Scaling Approach and Statistical Analysis

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Abstract

The ability of soils to sorb heavy metals is quantified by sorption isotherms. The field-scale variability of heavy metal sorption isotherms across fields of apparently “homogeneous” soil is often very large and makes the upscaling of point measurements to larger scales problematic. This may be overcome by scaling of sorption isotherms, which is a method that potentially reduces the wide spread of the isotherms into a reference or average isotherm, respectively, but preserves the variation through calculated scale factors. At two study sites near Hannover, Germany (loess soil at Lathwehren, loamy to sandy soil at Vinnhorst), we investigated the field-scale variability of the sorption isotherms of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn). For each site, 50 samples were taken along a 250 m transect at two depths. Further, for each site and depth a composite sample was mixed from aliquots of the 50 transect samples. Sorption isotherms of single heavy metals were measured, along with a range of soil properties, including pH, CEC, OC, and texture. The isotherms were successfully parameterized by the Freundlich equation and were spatially very variable. Calculation of scale factors for the sorption isotherms was successful, as scaling reduction of variance was high (from 64% to 99%). We then tested if correlations between scale factors of different heavy metal sorption isotherms, and also to soil properties existed. Such correlation were expected, because heavy metals (e.g. Cd and Zn) are competitively adsorbed, and the respective soil properties directly relate to ion sorption in soil. Significant correlations between scale factors of heavy metal sorption isotherms were only found at one site and depth (in the loamy to sandy subsoil). Thus, these relationships were site- and depth specific and are not generalizable. In addition, significant correlations between scale factors of heavy metal sorption isotherms and soil properties occurred only sporadically, and were not transferrable. One possible reason for this might be that the data were transformed (difference transformation) prior to correlation analysis to obtain normality.

A further objective was to prove, whether the average isotherms can be represented by a single measured isotherms of the composite samples from the area. This was found to hold at the loess site, but not at the loamy to sandy site. This indicates that scaling is favorable to sites not too much differing in soil texture. Although correlation analysis revealed only sporadic and not transferrable correlations, a multiple linear regression equation for the Lathwehren subsoil was found to predict Cu sorption scale factors from organic carbon content and cation exchange capacity. From our investigation we conclude that scaling is a useful tool to quantify and express field-scale variability of heavy metal sorption isotherms in soils. However, a prediction of scale factors from simple soil properties was only partly successful and needs further research efforts.

3.1.1 Introduction

Heavy metals can be found in almost every combustion process and in many industrial sources in the form of dust and gaseous emissions (Bradl, 2005). The Convention on Long-Range Transboundary Air Pollution (CLRTAP), held in 1979 by the United Nations Economic Commission for Europe (UNECE), aimed to gradually reduce and prevent air pollution, including heavy metals (Sands and Peel, 2012). Recently, certain data from the Federal Environmental Agency of Germany (one of the UNECE member countries) has shown that the amounts of cadmium, lead and mercury from air emissions, which were targeted by the CLRTAP Protocol, significantly decreased within the last two decades, whereas certain other heavy metals increased. For example, the emission of copper and zinc in 2011 increased by approximately 25.4% and 17.9%, respectively, compared to 1990 (UBA, 2013). The heavy metals from non-point source pollution (air emissions, fertilizer, waste disposal, etc.) are deposited on the Earth's surface (mostly the bare soils) across a large area (Violante *et al.*, 2007) and retained in the soil as a “chemical time bomb” (Stigliani *et al.*, 1991). These metals have the potential to harm environment and human health (Selim and Sparks, 2001; Alloway, 2012). During the heavy metal retardation process in the soil, a series of physical, chemical and biological processes are involved (Violante *et al.*, 2007). The evaluation of the existence and the behavior of this kind of heavy metal in soils within a large area is, however, an unsolved problem.

The main problem arises from the heterogeneity of soil (Heuvelink and Webster, 2001). The most significant process in heavy metal retardation in soil is the adsorption of these reactive substances. In other words, adsorptive bonding primarily controls the mobility and leaching danger in soils (Travis and Etnier, 1981). Literature studies have shown that the sorption of heavy metals varies strongly in soils, because of variation i.a. in soil pH, clay content, oxide content, and soil organic carbon content (e.g., Boekhold and van der Zee, 1992; Streck, 1993; Springob and Böttcher, 1998a, Altfelder *et al.*, 2007). Equilibrium models and kinetic models are the traditional ways to describe the sorption behavior in soils (e.g., Bruemmer *et al.*, 1986; Dube *et al.*, 2001), and simple adsorption isotherm equations are often used to model heavy metal adsorption in soils at low concentrations (Sposito, 2008). The classical equilibrium modeling is described by the Freundlich equation or the Langmuir equation, and the modeling is able to obtain the needed sorption information with a high degree of accuracy (Buchter *et al.*, 1989). However, the estimation of the sorption property is time consuming and expensive. Additionally, the non-linear function that describes the sorption also makes the quantification of field-scale variation difficult. Few studies have examined the relationship between measured soil properties and the sorption isotherms because there is no means to compare the single-valued property and the functional property directly. Consequently, the understanding of field-scale variation of heavy metal sorption is still limited.

A means of converting the non-linear into a linear relationship without changing the inherent variability is the so-called “scaling” method. Scaling has a long history and exists in various disciplines of natural science. It addresses the transformation of information across different spatial or temporal scales (Roth, 2008). One confirmed scaling theory was introduced by Miller and Miller (1956) in soil physics and represents one of the milestones in the area of soil water research (Raats and van Genuchten, 2006). Under the assumption of geometric similarity of the soil matrix, the soil water properties, such as pressure head (h) and hydraulic conductivity (K), are related to a corresponding characteristic length (r^*) by mathematical expression $h/h^* = r^*/r$ and $K/K^* = (r/r^*)^2$. The most attractive feature of scaling is the ability to describe the probability density distribution and the spatial structures of correlation using the scale factor α $(= r/r^*)$ (Vereecken *et al.*, 2007). Although scaling in soil physics research varies in technique (Tillotson and Nielsen, 1984), it has been confirmed as a convenient way to quantify spatially variable soil water characteristics (Roth, 1995; Wendroth *et al.*, 1999; Deurer *et al.*, 2001). Even more scaling can be used as an efficient tool for numerical research, which has been integrated into certain simulation programs of soil water flow and transport, such as HYDRUS (Simunek *et al.*, 2006).

Böttcher (1997) employed Millers’ scaling theory for the first time to scale Cd sorption isotherms. He demonstrated that the scale factors, which were calculated from the scaling procedure, could reduce the sorption isotherms to an average relationship, while also maintaining the variability for every single scale factor. In a subsequent study, a significant correlation between the scale factors of sorption isotherms of cadmium and zinc, measured by adsorption from single-metal solutions, was found (Böttcher, 1998). This correlation very probably results from the competitive sorption of these metal ions (e.g. Zemanová *et al.*, 2014). I.e. both metals adsorb to the same positions on soil particles, and thus, have the same adsorption variability. However, because these works were limited to a sandy soil and two heavy metals, further experimental investigation is needed to prove whether the relation between the scale factors is equal or biased systematically, and whether the finding of tightly related scale factors is valid for other heavy metals and other soils.

In this study, we investigated the field-scale variability of heavy metal sorption isotherms of Cd, Cu, Pb, and Zn in soils from two study sites (same extents, different variations), each with two soil horizons. Scaling was applied to simplify the description of the statistical variations in the sorption properties at the field scale. The first objective was to test the relationship of the scale factors of sorption isotherms between the different, mostly competitively sorbed heavy metals. Because Tillotson and Nielsen (1984) stated that scale factors “make it possible to examine the relationship between soil functions and easily measured, single valued soil properties”, the second objective was the comparison of the relationship between the calculated scale factors from the sorption isotherms of the heavy metals and the corresponding physical (clay content), chemical (pH, CEC, and oxides) and biological (organic carbon) soil properties. The third objective was to confirm, if the above-mentioned average relationship of isotherms can be represented with one single measured isotherm in a composite sample from the whole investigation area. Additionally, the accompanied uncertainty is evaluated from measurements, scaling procedures and site-specific variations. Finally, prediction of scale factors of sorption isotherms from soil properties using multiple linear regressions will be tested. As a possible result, a sufficiently certain quantification of the field-scale variation of heavy metal retention and mobility in soil may be obtainable from a combination of only a few of the expensive and time consuming measurements of heavy metal sorption, extensive measurements of soil properties, and calculation of scale factors of sorption isotherms from soil properties using multiple regression.

3.1.2 Material and Methods

3.1.2.1 Evaluation design

The evaluation design was organized as follows (Figure 3.1). In the first step, study sites for evaluating the field-scale sorption of heavy metals in soil were chosen, and sampling representing the field variability was performed. Second, laboratory measurements, including analyses of basic soil physico-chemical properties and sorption isotherms, were taken to ensure enough data for the following statistical analysis. Then, the scaling procedure was applied to both the basic properties and the sorption functions. Furthermore, three criteria from different

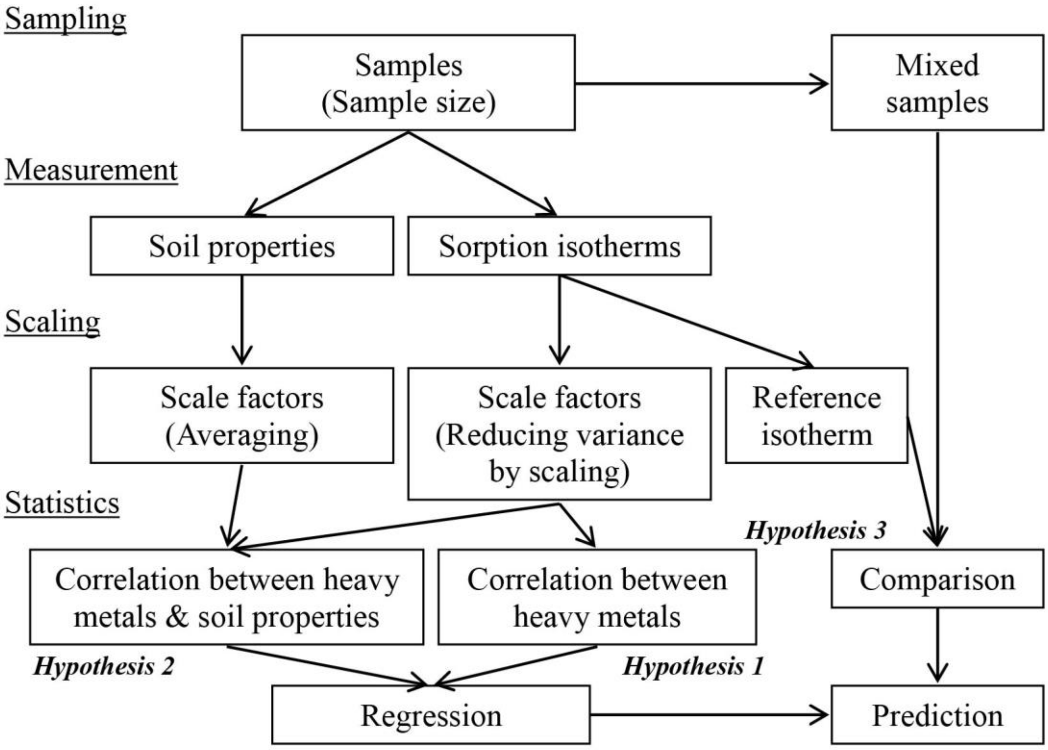

Figure 3. 1 Overview of the evaluation of field scale variability of heavy metal sorption isotherms in soil using scaling and statistical procedures.

viewpoints (sample size, averaging and reduction by scaling) were considered to validate the intensity of the soil survey and the efficiency of the scaling method. Last, the correlations and, if possible, regression analyses of the scale factors were examined.

3.1.2.2 Scaling of the sorption isotherm

Similar to other soil science or earth science data, the sorption properties of soils should also obey the central limit theorem as a continuous random variable, and the data can be statistically described by a probability density function (Caers, 2011):

$$P(a \leq X \leq b) = \int_a^b fx(x)\,dx. \tag{3.1}$$

However, in reality, the data were collected discretely from sampling points. For instance, the soil chemical property pH can be determined for *R* soil samples:

$$pH = (pH_1 \quad pH_2 \quad \cdots \quad pH_R). \tag{3.2}$$

With these data, a mean and a variance can be calculated to describe the distribution and variability of a given soil property. In statistics, the mean characterizes the central tendency. The variance describes the dispersion of a probability density function. Unfortunately, as shown in Section 2.2.1, the Freundlich sorption isotherms are quantified with two dependent parameters, which make the calculation of the mean and variance difficult. Therefore, the scaling method of Böttcher (1997) is adopted. Using these *R* samples as an example, *R* sorption isotherms can be measured and described by the Freundlich equation (Equation 2.2). At a certain absorbed amount S_1, the *R* residual concentrations *C* can be calculated from the *R* Freundlich equations and listed as

$$C_1 = (C_{1,1} \quad C_{1,2} \quad \cdots \quad C_{1,R}). \tag{3.3}$$

At a higher absorbed amount S_2, other R concentrations can be calculated and listed as

$$C_2 = (C_{2,1} \quad C_{2,2} \quad \cdots \quad C_{2,R}). \tag{3.4}$$

Thus, for *r (=1, 2 ... R)* sorption isotherms, a matrix can display the entire information of the sorption isotherms, if the number of *j (=1, 2 ... J)* absorbed amounts *Sj* is large enough:

$$\boldsymbol{C} = \begin{bmatrix} C_{1,1} & C_{1,2} & \cdots & C_{1,R} \\ C_{2,1} & C_{2,2} & \cdots & C_{2,R} \\ \vdots & & \ddots & \vdots \\ C_{J,1} & C_{J,2} & \cdots & C_{J,R} \end{bmatrix}. \tag{3.5}$$

The scale relationship for the residual concentration *C* in soil solution is

$$M_{j,r} = \alpha_{j,r}^2 C_{j,r}, \tag{3.6}$$

where *M* is the “scale mean” named by Simmons *et al.* (1979) and *α* is the scale factor, which makes a relationship between the mean and a single isotherm. The reason that the scale factor needs to be squared is given elsewhere (Böttcher, 1997, see scaling rule of sorption isotherms).

Thus, Equation (3.5) can be reformed as

$$\boldsymbol{C} = \begin{bmatrix} \frac{M_{1,1}}{\alpha_{1,1}^2} & \frac{M_{1,2}}{\alpha_{1,2}^2} & \cdots & \frac{M_{1,R}}{\alpha_{1,R}^2} \\ \frac{M_{2,1}}{\alpha_{2,1}^2} & \frac{M_{2,2}}{\alpha_{2,2}^2} & \cdots & \frac{M_{2,R}}{\alpha_{2,R}^2} \\ \vdots & & \ddots & \vdots \\ \frac{M_{J,1}}{\alpha_{J,1}^2} & \frac{M_{J,2}}{\alpha_{J,2}^2} & \cdots & \frac{M_{J,R}}{\alpha_{J,R}^2} \end{bmatrix}. \tag{3.7}$$

The principle of scaling is valid for a collection of *R* soil samples when the sorption similarity of Böttcher (1997) exists and the scale factors $\boldsymbol{\alpha_r}$ satisfy the scaling relationships (3.6) with the following constraint:

$$\frac{1}{R}\sum_{r=1}^{R} \boldsymbol{\alpha_r} = 1. \tag{3.8}$$

If the scale factors satisfy the normalization condition (3.8), then the scale means are given by

$$\frac{1}{\sqrt{M_r}} = \frac{1}{R}\sum_{r=1}^{R}\frac{1}{\sqrt{C_r}}. \tag{3.9}$$

After rearrangement, Equation (3.9) becomes

$$M_r = R^2\left[\sum_{r=1}^{R}\left(\sqrt{C_r}\right)^{-1}\right]^{-2}. \tag{3.10}$$

Hence, a reference isotherm can be computed from j points of the scale means. The scale factors $\boldsymbol{\alpha_r}$ are unknown, but a criterion must hold that each sorption isotherm has only one scale factor to the reference isotherm:

$$\begin{cases} \alpha_{1,1} = \alpha_{2,1} = \cdots = \alpha_{J,1} = \boldsymbol{\alpha_1} \\ \alpha_{1,2} = \alpha_{2,2} = \cdots = \alpha_{J,2} = \boldsymbol{\alpha_2} \\ \vdots \\ \alpha_{1,R} = \alpha_{2,R} = \cdots = \alpha_{J,R} = \boldsymbol{\alpha_R} \end{cases}. \tag{3.11}$$

For instance, the first rows of matrices (3.5) and (3.7) can be written as

$$\begin{bmatrix} C_{1,1} \\ C_{2,1} \\ \vdots \\ C_{J,1} \end{bmatrix} = \begin{bmatrix} \frac{M_{1,1}}{\boldsymbol{\alpha_1^2}} \\ \frac{M_{2,1}}{\boldsymbol{\alpha_1^2}} \\ \vdots \\ \frac{M_{J,1}}{\boldsymbol{\alpha_1^2}} \end{bmatrix}. \tag{3.12}$$

To facilitate the calculation, a transformation to natural logarithms can be made:

$$\begin{bmatrix} \mathrm{Ln}\, C_{1,1} \\ \ln C_{2,1} \\ \vdots \\ \ln C_{J,1} \end{bmatrix} = \begin{bmatrix} \ln M_{1,1} - 2\ln \boldsymbol{\alpha_1} \\ \ln M_{2,1} - 2\ln \boldsymbol{\alpha_1} \\ \vdots \\ \ln M_{J,1} - 2\ln \boldsymbol{\alpha_1} \end{bmatrix}. \tag{3.13}$$

Hence,

$$\sum_{j=1}^{J}\ln C_{j,1} = \sum_{j=1}^{J}\ln M_{j,1} - 2J\ln \boldsymbol{\alpha_1}, \tag{3.14}$$

and

$$\boldsymbol{\alpha_1} = \exp\left[(2J)^{-1}\sum_{\mathrm{j}=1}^{\mathrm{J}}\left(\ln M_{j,1} - \ln C_{j,1}\right)\right]. \tag{3.15}$$

Using the same algorithm, α_2 ... α_R can be calculated. Thus, the whole set of α_r is derived. This algorithm is only valid for the sorption processes that can be described with sorption isotherms, and this algorithm was used in this study. In other cases, in which the sorption isotherms could not be quantified with an empirical equation (Sposito, 2008), we suggest the use of the least square method of Warrick *et al.* (1990) (see approach 2 in Böttcher, 1997).

3.1.2.3 *Scaling of soil properties*

The soil properties also needed to be scaled to make the comparison of relationships meaningful. Similar to the calculation of the scale means from the sorption isotherms, the following relationship was applied to scale soil properties:

$$SP_m = \alpha_r^2 SP_r, \tag{3.16}$$

where SP_m is the scale mean of a soil property, SP_r is the measured value of this soil property at sampling point r, and α_r is the corresponding scale factor. The reason for the squared scale factor in Equation (3.16) is, that the respective soil properties form particle surface area in soil (OC, clay, oxides), or they are directly related to surface area (CEC, pH). And, as outlined in Böttcher (1997), phenomena related to surface area have squared scale factors.

Because certain soil properties, such as pH and CEC, are single values without functional dependences, the scale mean and scale factors can be simply derived from

$$SP_m = R^2 \left[\sum_1^r \left(\sqrt{SP_r}\right)^{-1}\right]^{-2}, \tag{3.17}$$

and

$$\alpha_r' = \sqrt{\frac{SP_m}{SP_r}}, \tag{3.18}$$

where α_r' is the non-normalized factor and should be converted under the normalization condition

$$\alpha_r = R\alpha_r' \left(\sum_r^R \alpha_r'\right)^{-1}. \tag{3.19}$$

3.1.2.4 *Uncertainty analysis*

When the scaling procedure is performed for such a nonlinear relationship, information must be lost because of the scaling. One disadvantage of scaling was determined by Oliveira *et al.* (2006); the scale factor could lead to underestimation of the true variability in the heterogeneous unsaturated flow field. Thus, more questions arise and can be generalized into the concept of “uncertainty”.

3.1.2.4.1 *Reduction by scaling*

Böttcher (1997) has stated that the sorption similarity likely does not exist in natural soils. Therefore, the scaling is not able to exactly reconstruct the variability of the sorption isotherm. It is necessary to formulate an expression that can be used to rate the efficiency of the scaling in a single value. This difference, which comes from the sum of the squares between individual data points and the reference isotherms, was defined as the “reduction by scaling” (*RS*) using the following equation:

$$RS = \frac{SS_{before} - SS_{after}}{SS_{after}}, \tag{3.20}$$

where *SS* refers to the sum of squares of natural logarithm deviations from the mean isotherm.

3.1.2.4.2 The problem of averaging

Scaling can be considered to be an averaging method from the small scale to the large scale, which has been widely discussed as “upscaling” the soil water problem. However, as stated in Zhu and Mohanty (2003), the different averaging methods may have different degrees of appropriateness in describing a heterogeneous situation. In addition to scale means, a series of averaging procedures for soil properties (arithmetic, geometric and harmonic mean) were applied to test the scaling results under the influence of different means.

The arithmetic mean is

$$SP_{Am} = \frac{1}{R}\sum_{r=1}^{R} SP_r \,. \tag{3.21}$$

The geometric mean is

$$SP_{Gm} = \sqrt[R]{\prod SP_r} \,. \tag{3.22}$$

The harmonic mean is

$$SP_{Hm} = \frac{R}{\frac{1}{SP_1}+\frac{1}{SP_2}+\cdots+\frac{1}{SP_R}} \,. \tag{3.23}$$

The corresponding scale factors can be calculated using Equations (3.18) and (3.19).

3.1.2.4.3 Sample size

When the distribution of a population is unknown, the sample size is crucial to deriving an accurate spatial description. If the sampling strategy is insufficient from the beginning, it will be difficult to obtain the true population depending on the distribution of sampling unless the sample size is increased. A useful criterion was summarized by Mulla and McBratney (1999) and further discussed by Webster and Lark (2013), who stated that the desired sampling number N is derived from

$$N = \frac{(t^2 s^2)}{d^2}, \tag{3.24}$$

where t is the tabulated value of Student's t-distribution (for instance, 1.96 within a 95% two-sided confidence interval), s is a preliminary estimate of the standard deviation and d is the deviation desired between the mean and the population. N was determined to judge the efficient size of samples for future sampling campaigns.

3.1.2.5 Statistical analysis

The data analyses were performed using SPSS 21 software in four steps:

1. The distributions of soil properties and sorption isotherms were described with classical statistics (arithmetic mean and coefficient of variation, CV) (was done in *Chapter 2*).
2. Normality tests were applied (Kolmogorov-Smirnov test). When the variables did not have normality, logarithm transformations or difference transformations of time series analysis were performed.
3. The correlations of scale factors between different heavy metal sorption isotherms were determined. The correlations of scale factors between sorption isotherms and soil properties were determined.
4. A multiple linear regression for each heavy metal was applied using the determined relationships between sorption isotherms and physico-chemical soil properties.

3.1.3 Results and Discussion

3.1.3.1 *Scaling results*

In Figure 3.2A, the 50 measured sorption data points for cadmium in the Lathwehren topsoil, for instance, were plotted together. After scaling, the points were close to the reference isotherm (Figure 3.2B), and the variability was preserved in the individual scale factors.

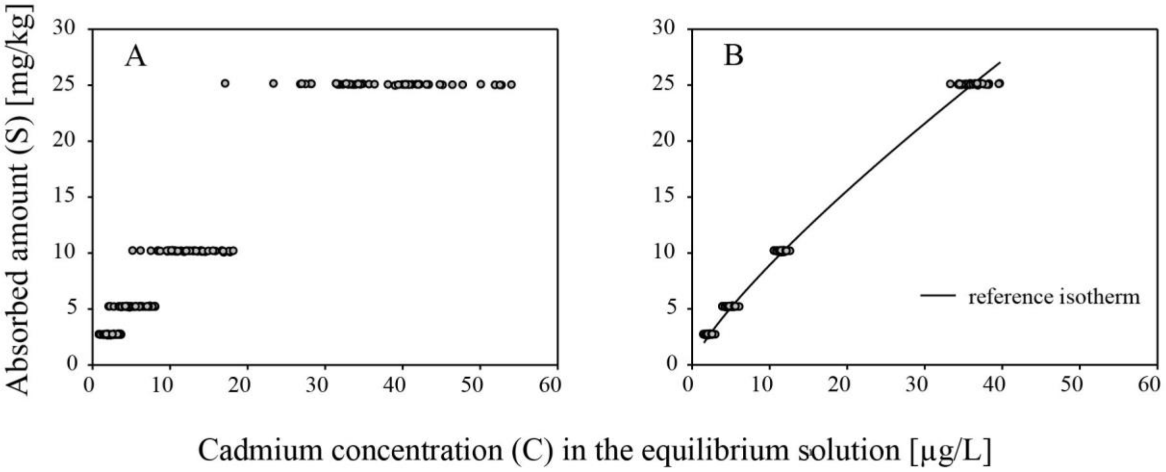

Figure 3. 2 Cadmium sorption isotherms for the 50 soil samples under study in the Lathwehren topsoil. A: Measured data before scaling. B: Data after scaling. The line shows the calculated reference isotherm.

Due to the definition of scaling, the calculated mean of a set of scale factors is always equal to one. Only the coefficients of variation are listed in Table 3.1. It is already known that the scale factors for Vinnhorst should have a larger span than those for Lathwehren, based on Tables 2.2 and 2.3. Three further statements can be made.

1. The scale factors of the sorption isotherm vary stronger than the scale factors of the soil

properties.

2. A similar order of magnitude of coefficients of variation (CV) between the different heavy metals (except copper) was observed in each horizon, which raises the question that the variability of sorption between heavy metals may be correlated.
3. The coefficients of variation of the soil properties' scale factors are similar to half of the CVs of soil properties. The cause of this is the squared relationship in Equation (3.6).

Table 3. 1 Coefficients of variations (CV) of the scale factors. A: At Lathwehren. B: At Vinnhorst.

CV [%]		α(Cd)	α(Cu)	α(Pb)	α(Zn)
A	Topsoil	12.7	5.0	18.4	14.4
	Subsoil	14.4	10.3	20.0	14.2
B	Topsoil	19.1	7.7	36.1	37.5
	Subsoil	91.1	62.7	94.1	99.2

CV [%]		$\alpha(H^+)$	$\alpha(CEC_{eff})$	α(OC)	α(clay)	$\alpha(Fe_{ox})$	$\alpha(Al_{ox})$	$\alpha(Mn_{ox})$
A	Topsoil	17.4	4.8	9.6	4.3	1.8	1.9	5.7
	Subsoil	15.0	8.2	12.5	7.0	2.6	3.2	8.3
B	Topsoil	51.2	9.6	9.5	12.9	12.0	13.5	13.9
	Subsoil	99.5	6.3	28.0	30.0	45.3	31.9	95.8

3.1.3.2 Uncertainty analysis

3.1.3.2.1 Reduction by scaling

After scaling, the reduction of *SS* is rather enormous, as shown in Table 3.2. An explanation how these reductions influence the correlation analysis in Section 3.1.3.6 can be found in Table 3.2. For instance, the reductions of the four heavy metals from the subsoil at Vinnhorst have the highest values (more than 88%) among the four horizons. This high reduction might be the reason why the scale factors of the heavy metals led to the high correlation with each other. Additionally, the finding in Section 3.1.3.1, which indicates that the scale factors between different heavy metals have the same order of magnitude, could also be attributed to the high correlation. However, we also noticed that the sum of squares after scaling in the Vinnhorst subsoil is even higher than the *SS* before scaling in other soil horizons, which indicates that some variability is not covered by the scale factors. This variability portion not covered by scaling depends on the variability of Freundlich *n* in relation to the variability of Freundlich *K*, as can be seen by the significant (P = 95%) correlation (r = 0.75) depicted in Figure 3.3. The reduction of *SS* by scaling decreases with increasing relative variability of *n*. The regression is confirmed by the two independent data points in Figure 3.3 (data of Böttcher, 1997, and Deurer and Böttcher, 2007) that were not included in the regression analysis. I.e., the relative variability of *n*, calculated by the ratio of CV% of *n* to CV% of *K*, is a suitable indicator of scaling uncertainty in terms of reduction of *SS*.

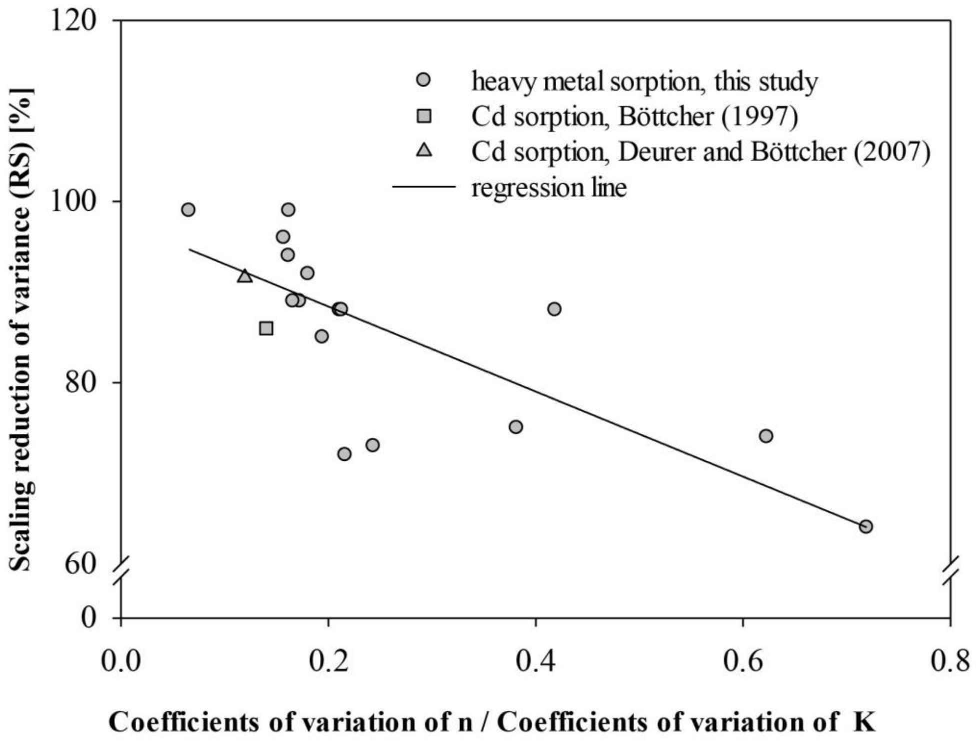

Figure 3. 3 Dependence of scaling reduction of variance on the relative variability of Freundlich parameter n (expressed by the ration of coefficients of variation (CV): CV n/CV K).

3.1.3.2.2 Different averaging procedures

Following the idea of comparing the reference isotherm with composite soil samples, the averaging procedure for soil properties was also investigated using different mean values. This analysis was performed with the methods introduced in Section 3.1.2.4.2. The different averaging methods could indeed generate different scale factors but do not affect the results of correlations in Section 3.1.3.5 and 3.1.3.6 (figures not shown). After normalization by Equation (3.19), the scale factors of different averaging procedures became identical.

Table 3. 2 Scaling reduction of sorption isotherms. SS: Sum of squares of natural logarithm deviations from the mean isotherm. RS: Scaling reduction of variance. A: At Lathwehren. B: At Vinnhorst.

A		SS_{before}	SS_{after}	RS [%]	B		SS_{before}	SS_{after}	RS [%]
Topsoil	Cd	20	3	85	Topsoil	Cd	55	14	73
	Cu	4	1	72		Cu	8	1	88
	Pb	80	29	64		Pb	158	7	96
	Zn	27	3	88		Zn	180	21	89
Subsoil	Cd	32	3	92	Subsoil	Cd	1458	10	99
	Cu	14	1	89		Cu	725	85	88
	Pb	85	22	74		Pb	2043	31	99
	Zn	34	8	75		Zn	2048	130	94

3.1.3.2.3 Sample size

As an example of sample size calculations, the mean of the scale factors of cadmium in the Vinnhorst subsoil is 1, and the standard deviation is 0.9 (Table 3.1). If the deviation, *d*, in Equation (3.24) is desired not to exceed 0.1, i.e., 10% of the mean, one would have to collect 312 samples. For $d \leq 0.2$, i.e., 20% of the mean, one would have to collect 78 samples. These results are obviously greater than the original 50 samples. From the statistical perspective, Jaccard and Becker (2002) also suggested the collection of more than 100 samples to avoid situations where some extreme outliers cause a large negative effect on the assumptions of normality or linearity. Thus, future sampling campaigns for evaluation of sorption variability should consider 80 to 100 samples per site.

3.1.3.3 Composite soil sample

As demonstrated in Böttcher (1997), the scaling can reduce the variability into an averaged relationship. At the design step of this investigation, we were aware that in addition to the scale factors, the reference isotherm is also important. The scale factors are useful for prediction or monitoring purposes only if it is associated with a reference isotherm. The mixing of soil samples may be a practical way to derive the reference isotherm. The sorption isotherms of the composite soil samples (topsoil and subsoil at Lathwehren and Vinnhorst) were compared with the reference or average isotherms, respectively, calculated from the scaling procedure. The results showed that the isotherm from the composite samples is located in a narrow range of the reference isotherm with respect to the whole field-scale variation at the Lathwehren site (texture: silt with only slight variation, Figure 2.1). For instance, in Figure 3.4A, the reference isotherm was close to the isotherm derived from the composite cadmium soil samples. However, a large deviation appeared at the Vinnhorst site (texture: broad range from loam to sandy loam, Figure 2.1), especially at higher concentrations (Figure 3.4B). This indicates that scaling is favorable to sites not too much differing in soil texture.

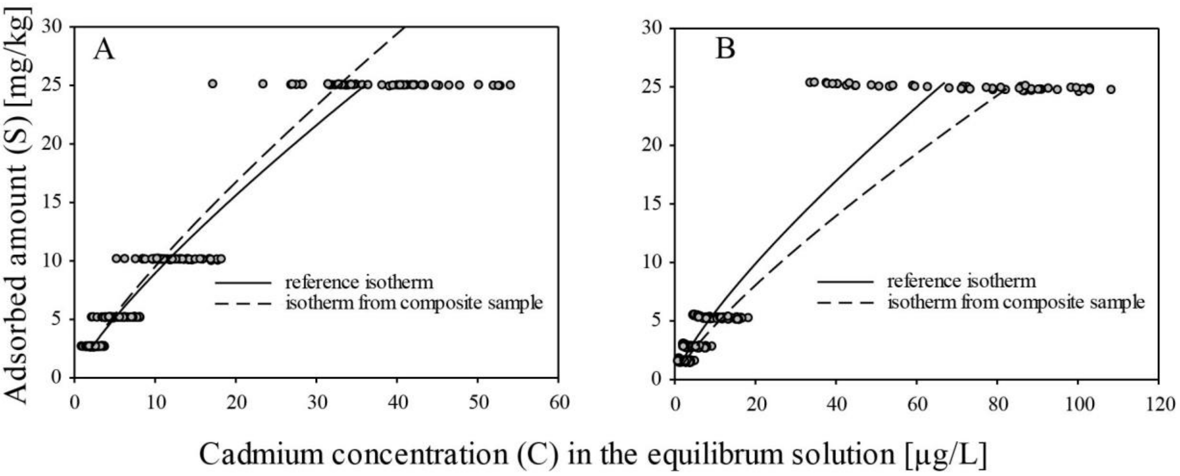

Figure 3. 4 Comparison of reference isotherm and the isotherm derived from the composite soil sample based on the sorption data. Solid line: reference isotherm; dashed line: isotherm derived from the composite sample. A: Cadmium in the Lathwehren topsoil, B: Cadmium in the Vinnhorst topsoil. Note the different scales of the X axes.

3.1.3.4 Site specific distribution

A precondition for calculation of Pearson’s correlation coefficients is that the scale factors of isotherms and soil properties should obey a normal distribution. For example, the scale factors of Pb sorption isotherms in the topsoil and subsoil of the Lathwehren site are normally distributed, which can be determined either readily from the histogram (Figure 3.5, A and B) or calculated by the Kolmogorov-Smirnov (KS) test. The asymptotic significances of the KS test were 0.55 for topsoil and 0.25 for subsoil. However, the scale factors of both the topsoil and subsoil at Vinnhorst are neither normally nor lognormally distributed (Figure 3.5, C and D). They show two central tendencies in the histogram, which means there are two modes at the Vinnhorst sampling transect. Nevertheless, similar to the texture of this site shown in Section 3.1, the scale factors of the Pb sorption isotherms were spatially continuous and varied with a tendency (Figure 3.5, G). To eliminate the influence of this spatial tendency, a first-order differencing transformation based on a time series analysis was performed as follows:

$$\Delta\beta = \beta_m - \beta_{m-1}, \tag{3.25}$$

where the factor $\Delta\beta$ is the difference between two adjacent data points β of m soil samplings. After the transformation, the distribution of α(Pb) was reinstituted as normality (Figure 3.5, E and F), and the asymptotic significance of the KS test reached 0.33 for topsoil and 0.06 for subsoil.

3.1.3.5 Correlation at Lathwehren

The scale factors between Cd and Pb and between Cd and Zn are relatively weakly correlated (Table 3.3A). Almost every heavy metal was correlated with the scale factor of soil pH (H^+ in Table 3.3). After removing an outlier, an even more meaningful result is that the coefficient of correlation between Cd and H^+ in the subsoil increased to $r = 0.811$. Thus, this correlation could be solid evidence indicating that the sorption is closely correlated to the soil chemical conditions. Another correlation was also found; Cu exhibited a correlation with effective CEC and organic carbon in both horizons. This was also found by Zhou *et al.* (2003), who explained the predominant interaction of soil organic matter with Cu at pH conditions above 6.8.

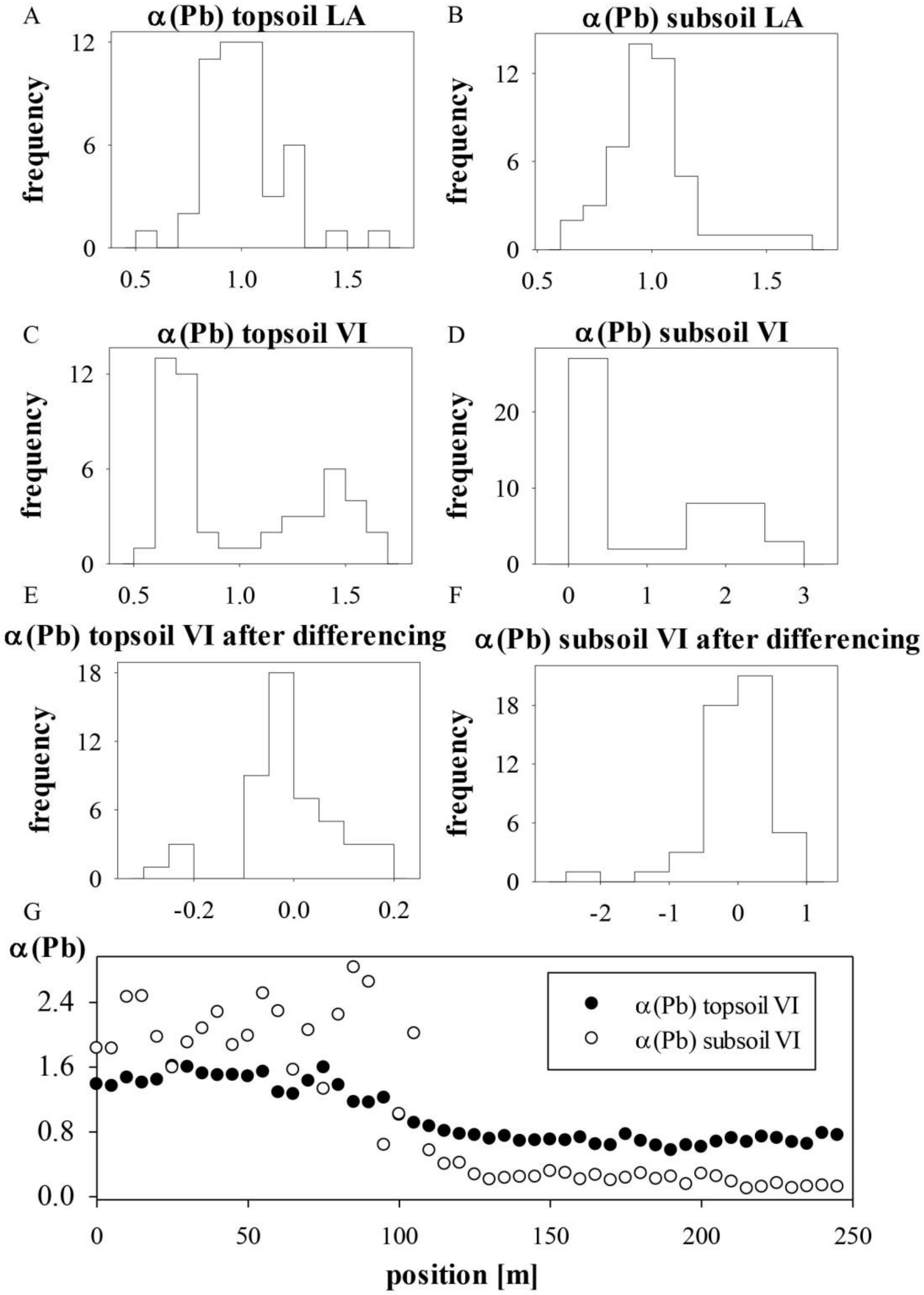

Figure 3. 5 Histograms of the scale factors in Lathwehren and Vinnhorst. Bell-shaped curve: normal distribution curve. A: *α*(Pb) for the Lathwehren topsoil, B: *α*(Pb) for the Lathwehren subsoil, C: *α*(Pb) for the Vinnhorst topsoil, D: *α*(Pb) for the Vinnhorst subsoil, E: transformed *α*(Pb) for the Vinnhorst topsoil, F: transformed *α*(Pb) for the Vinnhorst topsoil. G: scale factors of the Pb sorption isotherms along the Vinnhorst transect.

3.1.3.6 Correlation at Vinnhorst

As determined in Section 3.1.3.4, the scale factors at Vinnhorst were neither normally nor lognormally distributed. After differencing transformation, the data of topsoil at Vinnhorst were finally normally distributed. Among the heavy metals, only copper had a weak relationship with lead and zinc (Table 3.4A). The soil chemical property H^+ correlated with both cadmium and zinc. For other soil properties, Mn oxides had common relationships with three heavy metals; these relationships were not observed at Lathwehren. The scale factors in the subsoil of Vinnhorst varied much more than in any other soil horizon, which has already been shown in Table 3.1. The bimodal distribution was also more pronounced than in the topsoil. After transformation, certain soil property variables still could not be changed into a normal distribution. Thus, we decided to divide this horizon into two groups. The first group were observations from 0 to 110 m along the transect (see Figure 3.5, G). The second group were observations from 110 to 250 m distance. The scale factors of the heavy metals were normally distributed in both parts, but certain soil property scale factors still did not satisfy the conditions of normal distribution. The difference transformation was used once again to fix this problem. Finally, all scale factors were normally distributed, and the correlations are shown in Tables 3.4B and 3.4C. Mn oxide was correlated with most heavy metals. At the distance from 110 to 250 m, organic carbonate was also correlated with the heavy metals; this correlation was not observed in the first group. Strong correlations were found between every heavy metal scale factor. Because the same situation was not found in the topsoil, a partial correlation was performed to examine whether these correlations arise from site-specific influences or if they are indeed correlated. After examination, only the correlations between Pb and Cu and between Cd and Zn in the first 110 m and between Cd and Pb in the rest 140 m were significant at α=0.01.

We are compelled to note that an easily neglected problem was revealed by the testing for normal distributions. The KS test assumes the data are normally distributed as hypothesis H_0. Using the mean and variance, a normal distribution function is constructed and is calculated from the samples themselves. The significance between a sample value and the corresponding value calculated from the new normal distribution function is then used to test whether the hypothesis H_0 should be rejected or not. It can be strongly affected by the sample size and outliers. For instance, the non-transformed subsoil data from 110 to 250 m have a normal distribution in the KS test. In the correlation analysis, all scale factors were unexpectedly correlated. These findings could lead us to a wrong conclusion. Because the mean and variance come from the samples themselves, it is necessary to respect the effect of the degrees of freedom. The Lilliefors test, which is adopted in the KS test, and the Shapiro-Wilk (SW) test can be used when a sample size is < 50 (Vereecken and Herbst, 2004). The non-transformed data of samples 23-50 then demonstrated that they could not pass the Lilliefors or SW test.

3.1.3.7 *Prediction from easily measured soil properties*

The correlation analysis and the uncertainty analysis demonstrated considerable difficulty in capturing the field-scale variability of sorption with suitable accuracy. One possible reason for this might be the unavoidable data transformation (differencing). Certain valuable results were found after the regression analysis for the Lathwehren site. For instance, the regression of copper sorption in the Lathwehren subsoil was obtained from the correlation result in Section 3.1.3.5. A relationship between the scale factor of the Cu sorption isotherm, the OC and the CEC can be derived using the following equation:

$$\alpha_{Cu} = 1.027 + 0.62\alpha_{OC} - 0.651\alpha_{CEC}. \qquad (3.26)$$

Table 3. 3 Pearson's correlation coefficients between scale factors of heavy metal sorption isotherms and soil properties. A: Lathwehren topsoil. B: Lathwehren subsoil.

A	α(Cu)	α(Pb)	α(Zn)	α(H^+)	α(CEC_{eff})	α(OC)	α(Fe_{ox})	α(Mn_{ox})	α(Al_{ox})	α(clay)
α(Cd)		0.332*	0.499**	0.667**			-0.359*	-0.298*		
α(Cu)				0.428**	-0.424**	0.431**				
α(Pb)							-0.438**	-0.461**		
α(Zn)				0.675**						
B										
α(Cd)		0.306*	0.354*	0.655**					0.348*	0.279*
α(Cu)		0.373**		0.468**	-0.400**	0.543**	0.474**		-0.376**	
α(Pb)			0.297*	0.434**		0.548**				
α(Zn)				0.516**						

**: significant at P=0.01; *: significant at P=0.05 (double sites)

Table 3. 4 Pearson's correlation coefficients between scale factors (after difference transformation) of heavy metal sorption isotherms and soil properties. A: At the Vinnhorst topsoil. B: At the Vinnhorst subsoil, sample numbers 1-22. C: At the Vinnhorst subsoil, sample numbers 23-50.

A	α(Cu)	α(Pb)	α(Zn)	α(H^+)	α(CEC_{eff})	α(OC)	α(Fe_{ox})	α(Mn_{ox})	α(Al_{ox})	α(clay)
α(Cd)				0.384**	-0.313*			-0.422**		
α(Cu)		0.457**	0.337*					-0.370**		
α(Pb)				0.428**				-0.421*		
α(Zn)										
B										
α(Cd)	0.609**	0.584**	0.564**	0.465*				-0.619**		
α(Cu)		0.897**	0.674**					-0.641**		
α(Pb)			0.615**				-0.483*	-0.728**	0.513*	
α(Zn)				0.455*				-0.468*		
C										
α(Cd)	0.796**	0.901**	0.847**			-0.592**		-0.425*		
α(Cu)		0.838**	0.625**			-0.599**		-0.439*		
α(Pb)			0.801**			-0.386*		-0.440*		
α(Zn)					-0.574**	-0.513**	-0.386*	-0.444*		-0.410*

$^{\wedge}$ Data of Mn oxides are not transformed.

**: significant at P=0.01; *: significant at P=0.05 (double sites)

OC and CEC are two independent variables at this specific site, and they were detected by the principal component analysis and had no relationship in the correlation matrix. The determination coefficient R^2 is 0.52, which means that more than 52% of the variation in copper's scale factors is predictable using Equation (3.26). Furthermore, the isotherm from the composite samples is very close to the reference isotherm, as explained in Section 3.1.3.3. Based on these two conditions, a prediction of the field-scale variability of copper sorption can be made. A scatter plot of the predicted and the measured concentrations in the Lathwehren subsoil is shown in Figure 3.6. Certain comparable results demonstrated that by using the multiple regressions, the variation proportion of the Cd sorption parameter *K*, which could be explained by the basic soil properties, represents 44% of the total variation (Deurer and Böttcher, 2007) and only one-sixth in the study of Altfelder *et al.* (2007). However, in another study of the spatial variability of atrazine sorption parameters and other soil properties in a podzoluvisol, Jacques *et al.* (1999) concluded that these regressions have no meaning due to the low correlation coefficients.

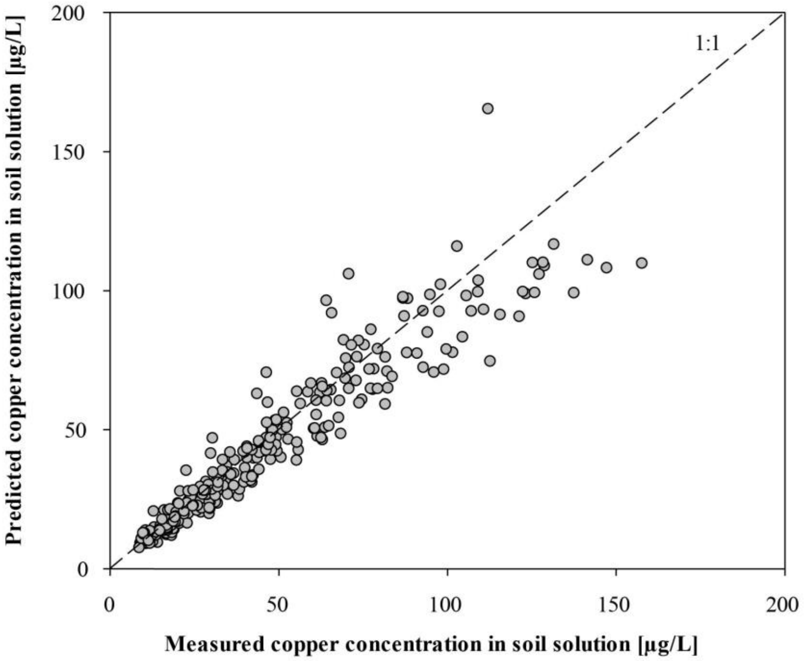

Figure 3. 6 Comparison between measured and predicted dissolved Copper concentrations in the Lathwehren subsoil.

3.1.4 Conclusions

This investigation showed that the variability of sorption isotherm parameters K and n was linearly related. The five conditions of Pearson's correlation test are strict for the collected data; thus, the evaluation has a certain subjective component. In one horizon at one study site, we did find a correlation of scale factors between the sorption of different heavy metals, which means that the first objective was satisfied under certain site specific conditions. We also found that the sorption of heavy metals in soil varied more strongly than all of the other measured soil properties. The variations in sorption were difficult to capture via the measured soil properties, which means that the second objective was not established. However, the regression analysis showed that the combination of the composite soil sample and the variation in measured soil properties could still describe the field-scale distribution of heavy metal sorption in soils. Hence, we conclude that scaling is a useful tool to quantify the variation of sorption isotherms at the field scale. Furthermore, the calculation of scale factors provides opportunities for spatial data analysis, which could be used to detect the spatial correlation structure of scale factors, and allows to use point measurements for geostatistical modeling (e.g. kriging, Nielsen and Wendroth, 2003). Especially the prediction of scale factors from simple soil properties needs improvement and thus, further research efforts.

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Chapter 4 Multivariate Geostatistical Analysis

4.1 The Scale Factors of Heavy Metal Sorption in Soils – Exploring Their Spatial Structural Correlations by Multivariate Geostatistical Analysis

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Keywords: heavy metal sorption, scaling, geostatistics, multivariate statistics, factorial kriging analysis.

Abstract

Taking two agricultural areas of Hannover, Germany, as case studies, we investigated the field-scale variability of heavy metal sorption in soil by the means of scaling and explored the hierarchical structure and nonstationarity of scaled sorption behaviour in space with other physico-chemical properties by multivariate statistics and geostatistics. The spatial structural relationships between scale factors of heavy metal sorption and soil properties were analysed with a linear model of coregionalization and principal component analysis according to the potential correlations at different scales. In one study region, nonstationary in the mean was observed and the data were transformed by residual maximum likelihood. Respecting particular correlation structures, all of these methods were applied to isolate and to display different sources of variation from small to large scale. In the first case study, the variogram of heavy metal sorption was fitted by three spatial structures, i.e. one nugget and two spherical scales. Unfortunately, the correlation between heavy metals was unusual at large scale and thus only two spatial structures remained. Nonetheless, the circles of correlation revealed a much stronger relationship between cadmium and zinc than ordinary correlation. Further study showed that the scaled soil physico-chemical properties were not correlated with heavy metal species at each nested scale. In the second case study in presence of nonstationary, the sorption of lead in soil was correlated to that of cadmium at the spatial-variation scale. The results indicate that the scaling can represent the spatial structures of soil sorption and relevant physico-chemical properties and multivariate geostatistical analysis is a meaningful way to reflect the principal features at different scales.

4.1.1 Introduction

Evaluation of the field-scale variability of heavy metal sorption in soils involves characterization of solute adsorption and transport properties in field soil. This has long been considered as a key problem in soil physics research (Vereecken *et al.*, 2016), because the soil properties controlling the transport and retention of water and reactive chemicals remain difficult to be measured and the measurements are time consuming (Degryse *et al.*, 2009). Furthermore, it is widely acknowledged that the architecture of soils varies in space considerably from the microscopic pore scale all the way up to the landscape/catchment scale (Pachepsky and Hill, 2017). More efforts are needed to develop scaling relations for a statistical characterization and averaging across soil structure, for instance, representative elementary volume in soil hydrology, to interpret hydraulic properties at larger scales (Jury *et al.*, 2011). An averaging means to define “effective” properties that represent the functional relationships between volume-averaged quantities, which are model and scale dependent (Durner and Lipsius, 2005). Soil science is currently limited by lack of understanding the importance of effective properties in a variety of heterogeneous soils. More and more sophisticated models have been used in the determination of transport and retention properties at all scales (Steefel *et al.*, 2015). However, before a suitable model is selected, a thorough understanding and characterization of soil structure and sorptional functioning and to relate structure and function in a model are still important steps. Therefore, quantitative description of physical, chemical, and biogeological interactions in soil at multiple scales represents a great challenge, particularly in terms of dealing with soil heterogeneity and model uncertainties.

The research into field-scale variability of reactive chemicals sorption in soils has been less intensive than studies of soil hydraulic properties. However, this field has received increasing amounts of interest in recent years not only in agricultural soil science but also in soil and environmental science (Jacques *et al.*, 1999; Steefel *et al.*, 2005; Carrillo-Gonzalez *et al.*, 2006; Miller *et al.*, 2010). The reactive chemicals usually include nutrients, pesticides, and heavy metals (Minasny and Perfect, 2004). Pesticides and heavy metals are today taken very seriously as contaminants from agricultural, industrial, and other sources (Šimůnek *et al.*, 2013). In addition, their sorption by soil components have been described with various empirical equilibrium models (distribution coefficients, and Freundlich and Langmuir adsorption isotherms) and chemical surface complexation models (Travis and Etnier, 1981; Goldberg *et al.*, 2007). For pesticide adsorption, the linear adsorption isotherm (distribution coefficient) is frequently applied because of its easy integration into various models (Wauchope *et al.*, 2002). However, it has been generally found that increased metal concentration increases sorption of heavy metal in soil, but the rate of increase decreases (Loganathan *et al.*, 2012). Consequently, non-linear isotherms such as Freundlich adsorption isotherm, as saturated sorption at greater loadings are most appropriate and the sorption is always related to soil properties. Therefore, soil scientists traditionally use pedotransfer functions to estimate sorption from soil properties for which data are more readily available (van der Zee and van Riemsdijk, 1987; Springob and Böttcher, 1998; Horn *et al.*, 2004; Minasny and Perfect, 2004).

Böttcher (1997) created a new avenue for delineating heavy metal adsorption in field soil that employs the Millers' scaling (1956) theory (see Pachepsky and Hill, 2017 for an extensive review). Regarding the assumption of geometric similarity of sorption results from microscopic particle systems, the soil sorption isotherm properties, namely adsorbed amount (S) and soil residual concentration (C), for i similar soils are related through a corresponding scale factor (α_i) by scaling rule for sorption isotherms of solutes in soils and thus, concentrations C_i can be transformed to a mean concentration C_m, by this single scale factor: $C_m = \alpha_i^2 C_i$ (Böttcher, 1997). Xiao *et al.* (2015) demonstrated that the scaling procedure could reduce the sorption isotherms to a scale-representative average or "effective" relationship at the field or management scale, meanwhile calculated scale factors could maintain the spatial variability of each sorption isotherm at the small scale or measurement points.

In our previous study (Xiao *et al.*, 2015), Pearson product-moment correlations, or simply ordinary correlations between scale factors of heavy metals and soil properties were discussed. We found that the sorption of heavy metals varied much more strongly than other measured soil properties, hence, use of the measured soil properties to predict sorption parameters was difficult. As stated by Wendroth *et al.* (2012), an individual stage of a process is relevant to the previous stage in a deterministic or a probabilistic way. Thus, a spatial soil process is the change of a variable or a state function consisting of multiple underlying effects or factors across a spatial domain. The relationships between soil properties may also vary in accordance with their spatial separation. Understanding these relationships is important in predicting sorption parameters from soil physico-chemical properties. Factorial kriging analysis was developed to solve such problems by combination of multivariate statistics and geostatistics (Goovaerts, 1992; Wackernagel, 2003). It is based on the theory of coregionalization and principal component analysis. Webster *et al.* (1994) were among the first to test factorial kriging analysis by revealing the spatial correlation of trace metals in the soil of the Swiss Jura. Castrignanò *et al.* (2000) investigated the spatial relationships among some soil physico-chemical properties of a field in central Italy. Nanos and Martin (2012) attempted to identify the source of heavy metal in soil in a Spanish river basin. However, this approach has not, in the soil science literature, been applied to characterize the relationships among soil sorption and other basic soil properties.

The aim of the present study was to reveal the spatial structural relationship between the calculated scale factors from the sorption isotherms of heavy metals (cadmium, copper, lead and zinc) and the corresponding soil properties (pH, organic carbon, oxalate extractable oxides and soil texture). The first objective was to explore the nested spatial structure of scale factors of sorption isotherms. A linear model of coregionalization was then applied, owing to the potential existence of common spatial structures at different scales. The second objective was to confirm, whether the ordinary correlation is enhanced by a scale-dependent analysis of the correlation structure among variables, where the principal components between scaled heavy metal sorption and physico-chemical soil properties were systematically checked. In addition, the residual maximum likelihood estimator was discussed for the variables with covariance structures that were not necessarily stationary. This motivated the last objective of this study, to assess the spatial structure of heavy metal sorption in soils after detrending and to identify their relations among heavy metals and soil properties at different scales of the whole area.

4.1.2 Material and Methods

4.1.2.1 Multivariate geostatistical analysis

Geostatistics has been introduced in soil science for almost 40 years, following initial work by Burgess and Webster (1980). Geostatistics has proven popular for solving problems in soil science areas such as determination of soil physical and chemical properties, experimental design and sampling methods including soil mapping, and soil quality management. Accordingly, soil scientists have benefited from these methods, especially after the explosive growth of powerful software in recent years. Several textbooks on geostatistics including soil science content are available (e.g. Goovaerts, 1997; Webster and Oliver, 2007; Chilès and Delfiner, 2012).

As long as one soil sample is taken, a number of soil parameters can be measured either in the field or in the laboratory. Sometimes all of these soil parameters need to be analysed together when geostatistical methods are used in determination of the spatial structure. Multivariate geostatistical analysis always starts from assuming *i* regionalized variables, known as random functions $Z_i(x)$. All these variables are defined over a domain *D* of $\mathbb{R}^n$:

$$\{Z_i(x) : x \in D \subset \mathbb{R}^n\}. \tag{4.1}$$

We say multi random functions are joint second-order stationary, when they satisfy the following two conditions. The first is characterized by their means:

$$\mathrm{E}[Z_i(x)] = m_i. \tag{4.2}$$

The second is the existence of covariance. In multivariate cases (e.g. for variables *i* and *j*), the direct and cross-covariances *C(h)* of *i* and *j* are expressed in matrix form:

$$\mathrm{C(h)} = \mathrm{Cov}\big[Z_i(x), Z_j(x+h)\big] = E\big[\{Z_i(x) - m_i\}\{Z_j(x+h) - m_j\}\big], \tag{4.3}$$

where *h*, known as the lag, is the spacing between measurement points *x* and *x* + *h*. When *h=0*, *C(h)* becomes the classical variance-covariance matrix *V*, that is

$$\mathrm{C}(0) = \mathrm{E}[\{Z_i(x) - m_i\}^2] = V. \tag{4.4}$$

In a weaker condition, namely joint intrinsic hypothesis for these *i* random functions, their direct and cross-variograms matrix *Γ(h)* could also be derived in the form of

$$\boldsymbol{\Gamma(\mathrm{h}) = \frac{1}{2}\mathrm{Cov}\big[\{Z_i(x+h) - Z_i(x)\}\{Z_j(x+h) - Z_j(x)\}\big].} \tag{4.5}$$

where *C(h)* and *Γ(h)* are functions of the lag and the lag only. The relationship between the cross-variogram and the cross-covariance, when it exists, is as follows:

$$\boldsymbol{\Gamma(\mathrm{h}) = \mathrm{C}(0) - \frac{1}{2}[C(h) + C(-h)].} \tag{4.6}$$

Goovaerts (1992) and Wackernagel (2003) both assumed that the correlation between *Z(x)* and *Z(x+h)* disappears if the lag h goes to infinity, i.e. *C(h)* and *C(-h)* become to zero. From Equations (4.4) and (4.6), the following relation between the variogram and the variance-covariance is derived:

$$\Gamma(\mathrm{h}) \rightarrow V \qquad for\ |h| \rightarrow \infty. \tag{4.7}$$

This is the important foundation for the theories given in Sections 2.2, 2.3, and 2.4. A soil process can operate and interact in terms of a mixed effort from different soil properties (Webster and Oliver, 2007). Each soil property has its own spatial structure (Cambardella *et al.*, 1994). This means that the spatial variation of this process could simultaneously occur on scales by different orders of magnitude. This so-called nested or hierarchical spatial structure can be observed through the nested variogram function, i.e. a special form of *Γ(h)* (Goovaerts, 1999). Then the classical variance-covariance matrix *V* could be replaced by this nested form of *Γ(h)*, since the mixture of different correlation structures is now separately analysed.

4.1.2.2 Coregionalization matrix and linear model of coregionalization

In a geostatistical framework, a regionalized process could be thought of as being the sum of several independent subprocesses simultaneously occurring at different characteristic scales. At each scale, a random function exists with its own covariance function or variogram. These functions build up this process together linearly (Goovaerts, 1992):

$$\gamma(h) = \gamma^{0}(h) + \gamma^{1}(h) + \cdots + \gamma^{S}(h), \tag{4.8}$$

where *γ(h)* is the variogram and formed as a combination of two or more, here *S*, individual variograms.

If an assumption is made that those processes are uncorrelated then Equation (4.8) could be represented by the sum of S normalized variograms:

$$\gamma(h) = \sum_{k=0}^{S} b^k g^k(h), \tag{4.9}$$

where $g^k(h)$ is the kth normalized variogram function and b^k is a coefficient that measures the relative contribution of the variance of $g^k(h)$ to the sum.

The equations described above represent the univariate circumstance of the nested variogram model known as linear model of regionalization. It can be expanded to multivariate form by using matrix notation, after which Equation (4.9) becomes

$$\Gamma(h) = \sum_{k=0}^{S} B^k g^k(h). \tag{4.10}$$

where $\Gamma(h)$ is the $i \times i$ variogram matrix for these i random functions and B^k is a positive semi-definite matrix of coefficients b^k known as a coregionalization matrix. This is the form of linear model of coregionalization. Through Equation (4.7) and (4.10), the classic variance-covariance matrix V is turned into several coregionalized variograms at different characteristic scales. Experimentally the variogram functions are nested, and based on the principle of parsimony and potential instability, S should not be more than 3 (Goovaerts, 1992).

4.1.2.3 Analysis of correlation structure

The statistical correlation function is a special expression of covariance between two variables, $Z_i(x)$ and $Z_j(x)$ (Wassermann, 2004). Normalizing the covariance function yields the classic correlation function:

$$\rho_{ij} = \frac{Cov\left[Z_i(x), Z_j(x)\right]}{\sqrt{Var[Z_i(x)] \cdot Var\left[Z_j(x)\right]}} = \frac{\sigma_{ij}}{\sigma_i \cdot \sigma_j}, \tag{4.11}$$

where ρ_{ij} is the coefficient of correlation. However, this correlation dose not account for the spatial aspect that may exist between observations. The coefficient of codispersion was introduced by Matheron (1965) as an interpretive tool to analyse the spatial correlation between the variations of $Z_i(x)$ and those of $Z_j(x)$:

$$\rho_{ij}(h) = \frac{Cov\left[Z_i(x) - Z_i(x+h), Z_j(x) - Z_j(x+h)\right]}{\sqrt{Var[Z_i(x) - Z_i(x+h)] \cdot Var\left[Z_j(x) - Z_j(x+h)\right]}} = \frac{\gamma_{ij}(h)}{\sqrt{\gamma_{ii}(h) \cdot \gamma_{jj}(h)}}. \tag{4.12}$$

For the data sets with a spatially hierarchical structure, a structural correlation coefficient could be derived:

$$\rho_{ij}^k = \frac{Cov\left[Z_i^k(x) - Z_i^k(x+h), Z_j^k(x) - Z_j^k(x+h)\right]}{\sqrt{Var[Z_i^k(x) - Z_i^k(x+h)] \cdot Var\left[Z_j^k(x) - Z_j^k(x+h)\right]}}$$

$$= \frac{\gamma_{ij}^k(h)}{\sqrt{\gamma_{ii}^k(h) \cdot \gamma_{jj}^k(h)}} = \frac{b_{ij}^k}{\sqrt{b_{ii}^k \cdot b_{jj}^k}}. \tag{4.13}$$

This coefficient of structural correlation reflecting the relationship between the two variables no longer depends on the lag h, instead, at the different hierarchical structures. In this way, the most effective correlation coefficient could be found, which is hidden in the classical correlation coefficient and is more pedologically plausible.

4.1.2.4 Principal component of coregionalization matrices

The idea of combining multivariate statistics, here specifically principal component analysis, to analyse linear model of coregionalization was proposed by Matheron (1982) and was introduced by Goovaerts (1992) into soil science. This approach is known as factorial kriging analysis. This analysis can be used for kriging or cokriging of a particular component on the basis of random functions, or for analysis of a multi-dimensional spatial vector in the same spirit as principal component analysis (Chilès and Delfiner, 2012).

Principal component analysis is a linear factor analysis method based on the mathematical concept of eigenvalues and eigenvectors and is widely used because of its simple algebra and straightforward interpretation. The variance-covariance structure of a set of variables can be explained through a few linear combinations of these variables to reach the goals of data reduction and interpretation. More detailed theory can be found in Johnson and Wichern (2007) and Wackernagel (2003).

A linear model of coregionalization is thought to be associated with an orthogonal decomposition of the form:

$$Z_i(x) = m_i(x) + \sum_{k=0}^{S} \sum_{v=1}^{p} A^k(i,v) Y_v^k(x) \,. \tag{4.14}$$

Here, $Y_v^k(x)$ are uncorrelated random functions, with zero mean and a variogram, which is proportional to the same normalized variogram $g^k(h)$ with a factor A^k. The expression of this variogram of any pair of variable i and j is

$$\gamma_{ij}(h) = \sum_{k=0}^{S} \sum_{v=1}^{p} A^k(i,v)\, A^k(j,v) g^k(h) \,, \tag{4.15}$$

and combining Equations (4.10) and (4.15) yields:

$$B^k = \sum_{v=1}^{p} A^k(i,v) A^k(j,v) = A^k (A^k)^T . \tag{4.16}$$

The only preliminary requirement of this equation is that B^k must be positive definite, which makes A^k infinite solutions. A natural determination of the matrices A^k could be conducted with principal component analysis, following which a new orthonormal coordinate system diagonalizing B is defined as (Chilès and Delfiner, 2012):

$$B = \sum_{v=1}^{P} \lambda_v u_v u_v^T, \qquad I = \sum_{v=1}^{P} u_v u_v^T, \qquad u_i^T B u_v = \lambda_v \delta_{iv}, \tag{4.17}$$

where λ_p are the eigenvalues of the covariance matrix B, u_p are the associated eigenvectors and u_i are the principal axes when $u_i^T u_v = \delta_{iv}$.

Webster *et al.* (1994) formulated a coefficient of correlation between a component and a variable, which is known as a “loading” in the principal component framework:

$$\rho = \frac{A_i^k}{Var[Z_i^k(x)]} = \frac{\sqrt{\lambda_v} u_{iv}}{\sigma_i}. \tag{4.18}$$

This correlation can be used to produce a plot known as a “circle of correlations”. The circle of correlations suggest that the loadings will be positioned on a circle, when the data are represented by only two components and the loading’s sum of squares is equal to one. Usually the variables are positioned inside the circle on the surface by two axes made from the first two principal components. Thus, the closer variables are to the centre of the plot, the less relevant they are to the first two components. The novelty of using principal component analysis after estimation of linear model of coregionalization is to enable an analysis of the correlation structure between variables for each nested scale rather than the raw observations. In particular, analysis can be conducted for each coregionalization matrix B^k instead of the covariance matrix V across the scales.

4.1.2.5 Stationary versus trend

A natural resource is unlikely to be always stationary in the mean, especially soils, which are known for their high heterogeneity. In geostatistics, this non-stationarity is called “external drift” or “trend in space”, to which different kriging methods e.g. universal kriging or kriging with an external drift are applied. Kriging methods are actually all forms of the empirical best linear unbiased predictor based on the linear mixed model (Lark., 2012). Cressie (1993) suggested that regionalized variables of Equation (4.1) may be modelled as a collection of random variables, generated by the random process:

$$Z(x) = \sum_{l=1}^{q} \beta_l \, z(x) + \varepsilon(x), \tag{4.19}$$

where *z(x)* is a collection of q nonrandom explanatory variables, β represents the coefficients marked as fixed effects, and ε is an error process. This general linear model could be written in matrix and vector notation as:

$$z = X\beta + \varepsilon, \tag{4.20}$$

and to solve it the likelihood function of the data from n observations

$$W \equiv [Z(1) - Z(2), Z(2) - Z(3), \ldots, Z(n-1) - Z(n)]^T \tag{4.21}$$

should be maximised. Equivalently, the negative log-form should be minimised, which may be written as (Lark and Cullis, 2004):

$$L_W(\beta, \theta) = constant + \frac{1}{2}\log|\beta| + \frac{1}{2}(W - A^T X\beta)^T (A^T \textstyle\sum(\theta) A)^{-1} (W - A^T X\beta), \tag{4.22}$$

where A is an element matrix. Residual maximum likelihood, normally known as “detrending” for processing a time series, is adopted to estimate θ from minimizing Equation (4.22). This estimator is accessed by implementing maximum likelihood to error contrasts in place of the data themselves. Lark *et al.* (2006) expanded Equation (4.20) as a linear mixed model with geostatistical meaning:

$$z = X\tau + Zu + \varepsilon, \tag{4.23}$$

where $X\tau$ refers to a fixed effect, e.g. unknown mean or coefficients of a trend in the geostatistical context, Zu is a random effect representing the spatially dependent random variation, and ε is independent random error as nugget variation in geostatistics. The relation between the target variable and the relevant variables and the variogram of the residuals could be estimated simultaneously based on this regression by residual maximum likelihood.

4.1.2.6 Data basis and analysis

Soil samples were taken from agricultural areas of Hannover, Germany (Lathwehren and Vinnhorst). A total of 100 topsoil samples were taken along a 250-m transect at 5 m intervals (50 samples from each site) and were subsequently air dried. The sorption isotherms of heavy metals including cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) and a range of soil physical (clay content), chemical (pH and oxides), and biological (organic carbon) properties were then measured. The scale factors of sorption isotherms (α_{iso}) and the scale factors of soil properties (α_{sp}) were calculated. The sampling and analytical procedures are described in detail by Xiao *et al.* (2015). In this study, α_{iso} and α_{sp} were evaluated by geostatistical means. The key contrast between the two sampling sites from the spatial statistics aspect was the pronounced nonstationarity in the mean observed at Vinnhorst. Therefore, we decided to treat these two sites as two case studies.

In Case Study 1 (Lathwehren), the data were decomposed at three characteristic spatial scales with the linear model of coregionalization. Three characteristic scales were experimentally defined based on the hierarchical variogram models as nugget scale, small scale with short range a_1, and large scale with long range a_2. Their coregionalized model could be written in the form

$$\gamma(h) = b_0\, \gamma_{nugget}(h) + b_1 \gamma_{spherical1}(h, a_1) + b_2 \gamma_{spherical2}(h, a_2), \tag{4.24}$$

where γ_{nugget} and $\gamma_{spherical}$ are authorized spatial models, which refers to the pure nugget and spherical model, respectively. The variograms of these two models are

$$\gamma_{nugget} = \begin{cases} 0 & for\ h = 0 \\ C_0 & for\ h > 0 \end{cases} \tag{4.25}$$

and

$$\gamma_{spherical} = \begin{cases} c\left\{\dfrac{3h}{2a} - \dfrac{1}{2}\left(\dfrac{h}{a}\right)^3\right\} & for\ h \leq a \\ c & for\ h > a \end{cases}. \tag{4.26}$$

In Case Study 2 (Vinnhorst), the data were also decomposed by the residual maximum likelihood. After detrending, three spatial structures were dissociated into nugget, trend, and spatial variance. The data analyses were performed using R with specialised packages. Among existing packages, we used RGeostats (Renard *et al.* 2018) for the calculation of variograms and fitting variograms to linear coregionalization models. GeoR (Ribeiro and Diggle 2001) was used to apply the residual maximum likelihood. Principal component analysis, which needs no specific package, was carried out after estimation of spatial structure to plot the circle of correlations.

4.1.3 Results and Discussion

4.1.3.1 Case Study 1 (Lathwehren dataset)

4.1.3.1.1 Variogram and fitting with authorised model

Semivariances were calculated from the scale factors of sorption isotherms and the scale factors of soil properties for a given distance (5 m in this study). Figure 4.1 is an example of the experimental variogram, in which the points are the calculated semivariances of α_{iso} of Cd along the transect. The dashed line represents the total variance (here 0.016 for Cd). It was found that these experimental points were not monotonically increased with increasing lag distance. The semivariance decreased at about 30 or 35 m after its initial increment and increased again at 80 m. An assumption could be made that a hierarchical structure might exist. The experimental variogram was later fitted with a nested model as the sum of a nugget effect and two spherical schemes with ranges of 35.1 and 115 m. The spatial structure's proportion of total variance was marked by different colours in Figure 4.1. The data show that the spatial structure represented 28% of total variance at nugget scale (illustrated by red colour in Figure 4.1), 64% at small scale (green), and 8% at large scale (blue). Note that the variation represented by spatial structure at small scale was eight times the variation at large scale. Moreover, almost one-third of the variance is included in the nugget effect, which means sorption of Cd in soil might not be as continuous as suggested in our previous study (Xiao *et al.*, 2015).

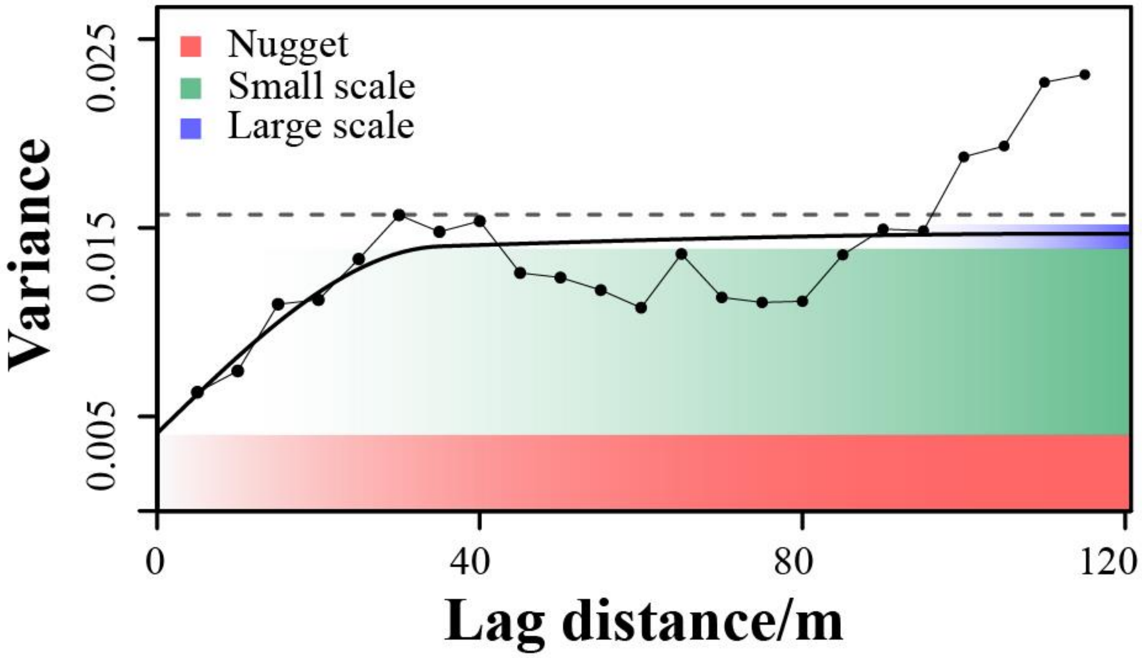

Figure 4. 1 Auto-variogram of sorption isotherms (α_{iso}) of cadmium in a 250-m transect (50 samples) in Case Study 1 (Lathwehren). The solid line is fitted model with three spatial structures (nugget, small-scale variance at range 35.1 m, and large-scale variance at range 115 m). The dashed line is the sill.

4.1.3.1.2 Auto- and cross-variograms

The other three heavy metals show similar auto-variograms of scale factors of sorption isotherms to that of Cd, except Pb (Figure 4.2), in which Zn and Cu stop increasing at small scale (about 30 m) and then increase again at large scale. This similarity suggests that all heavy metals were coregionalized to some degree. The dashed lines representing the total variance of each variogram show that Cu had the smallest variation (0.0025), Pb had the largest (0.04), and that of Zn (0.021) was similar to the total variance of Cd (0.016). Unlike those of Cd and Cu, the auto-variograms of Zn and Pb resemble one another as the nugget scale contains a large proportion of total variance. In contrast to auto-variograms, cross-variograms (Figure 4.3) between heavy metals showed much smaller sample covariances and the discontinuity between experimental points was more apparent.

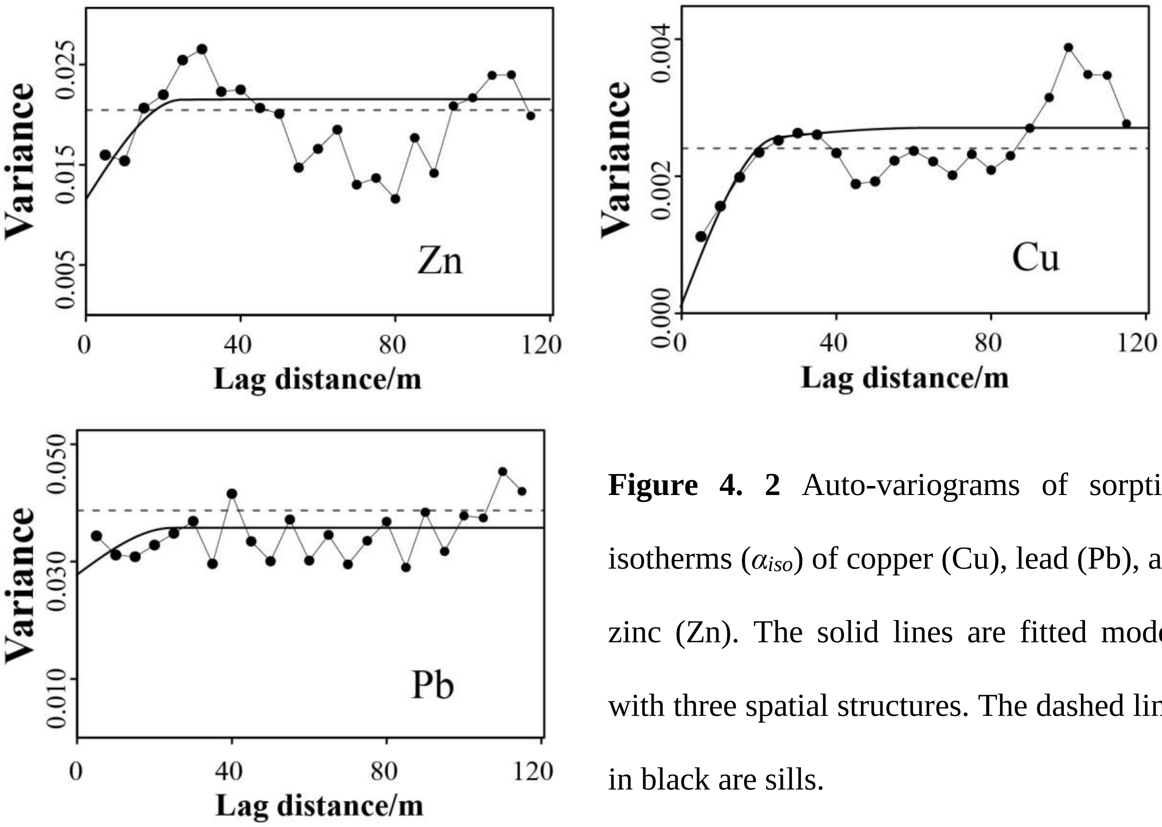

Figure 4. 2 Auto-variograms of sorption isotherms (α_{iso}) of copper (Cu), lead (Pb), and zinc (Zn). The solid lines are fitted models with three spatial structures. The dashed lines in black are sills.

4.1.3.1.3 *Linear models of coregionalization*

Linear models of coregionalization were also superimposed on the experimental points in Figures 4.2 and 4.3. The short range of small-scale variation after the running of the automatic fitting program was 24.9 m and the long range of large scale was 63.4 m. They were both smaller than the single fitted variogram of Cd, for which the ranges were 35.1 and 115 m, respectively. Furthermore, the long-range structures of both auto- and cross-variograms in Figures 4.2 and 4.3 are not as recognisable as in Figure 4.1. Criteria were selected to judge the

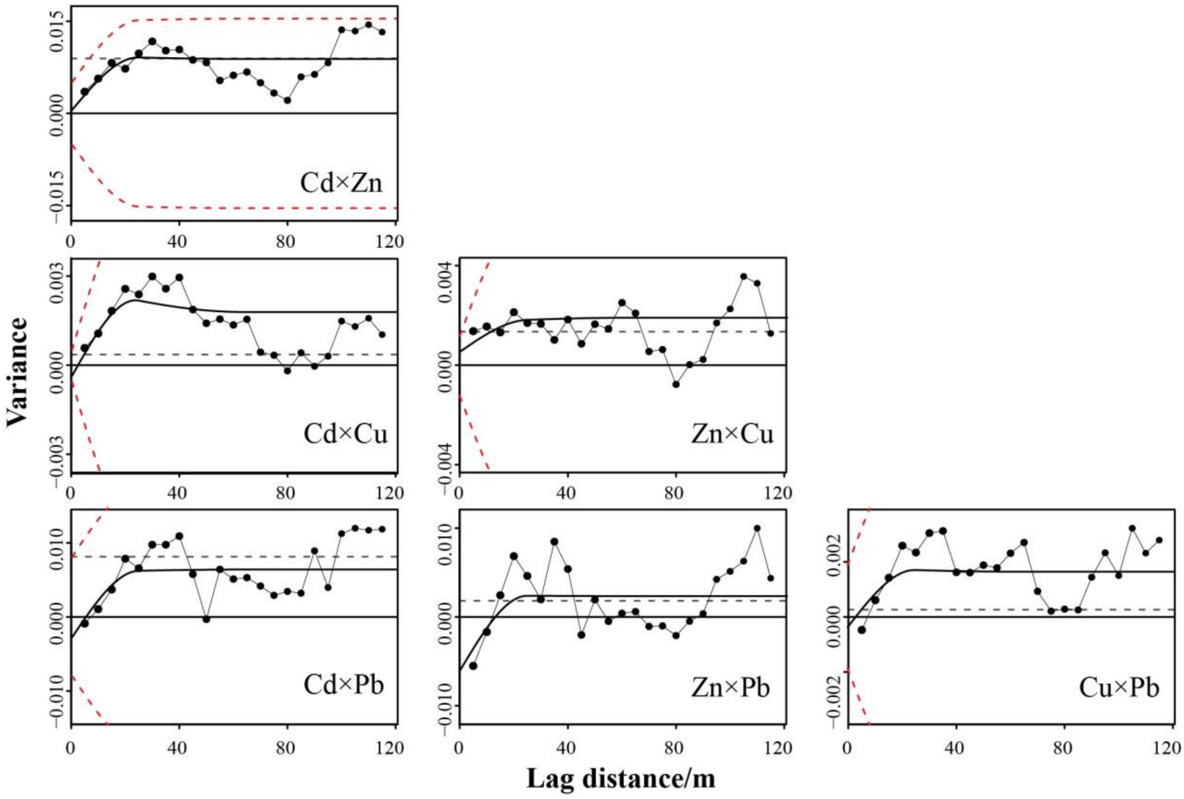

Figure 4. 3 Cross-variograms of sorption isotherms (α_{iso}) between cadmium (Cd), zinc (Zn), copper (Cu), and lead (Pb). The solid lines are fitted models of linear coregionalisation with three spatial structures (nugget, small scale variance at range 24.6 m, large scale variance at range 62.4 m). The black dashed lines represent sills. The red dashed lines represent the hulls of perfect correlation for the cross-variograms.

goodness of the fit of a variogram model to an experimental variogram. The red dashed curves on the upper and lower sites of the cross-variograms in Figure 4.3 represent the perfect positive and negative correlation, known as the "hull of perfect correlation" (Wackernagel, 2003). It is defined by the square root of the first fitted sills of the corresponding auto-variograms, where the sills b_{ij} of the cross-variogram are replaced by:

$$\mathrm{hull}\left[\gamma_{ij}(h)\right] = \pm \sum_{k=1}^{S} \sqrt{b_{ii}^{k} b_{jj}^{k}} \, g^{k}(h)\,. \tag{4.27}$$

The hull was originally designed to illustrate an improved variogram fitting with a visually high goodness of fit based on proximity of the line of the model to the experimental points. In this study, the proximity of the cross-variogram to the hull could be used to reveal some relationships. The two dashed curves are close, indicating significant cross-correlation. In contrast, the correlation is weak when the cross-variogram lies far from the bounds. As shown in Figure 4.3, only the cross-variogram between Cd and Zn had a relatively small hull. This is supported by the Pearson’s relationship (Table 4.1A), for which that the correlation coefficient between scale factors of Cd and Zn was 0.5.

4.1.3.1.4 Spatial structural correlation

The ordinary product-moment correlations of scale factors of sorption isotherms between heavy metals and their correlations with the scale factors of soil properties are presented in Table 4.1A. As mentioned above in Section 4.1.3.1.3, the scale factors of sorption isotherms between Cd and Zn were weakly correlated. For such variety of soil properties, only the scaled soil pH had a weak correlation with Cd and Zn. After estimation of linear coregionalized models, the ordinary product-moment relations between the whole multivariate properties can be represented by their nugget and structural correlations (Table 4.2). The correlation at the small and large scales were both enhanced comparing to the Pearson's correlation coefficients. However, the correlations at the large scale seemed unusual, as all heavy metals were perfectly positively or negatively correlated.

Table 4. 1 Correlation coefficients of scale factors between heavy metal sorption isotherms and soil properties. A: At Case Study 1 (Lathwehren). B: At Case Study 2 (Vinnhorst).

A	α(Cu)	α(Pb)	α(Zn)	α(H^+)	α(OC)	α(Fe_{ox})	α(Mn_{ox})	α(Al_{ox})	α(clay)
α(Cd)	0.06	0.33	0.5	0.67	-0.33	-0.36	-0.3	-0.05	-.0.8
α(Cu)	1	-0.51	0.19	0.43	0.43	0.27	0.07	0.06	-0.05
α(Pb)	-0.51	1	0.01	0.12	0.01	-0.44	-0.46	-0.09	0.28
α(Zn)	0.19	0.01	1	0.68	0.07	-0.06	-0.19	-0.27	-0.07
B									
α(Cd)	0.13	0.09	-0.08	0.38	0.08	-0.1	-0.42	0.09	-0.13
α(Cu)	1	0.46	0.34	0.27	-0.02	-0.11	-0.37	-0.22	-0.16
α(Pb)	0.46	1	0.02	0.43	0.05	-0.28	-0.42	0.03	-0.03
α(Zn)	0.34	0.02	1	0.15	0.19	-0.05	-0.13	-0.01	0.05

Table 4. 2 Correlation coefficients of Case Study 1 (Lathwehren) between scale factors of heavy metal sorptions at A: nugget scale, B: small scale and C: large scale.

A	α(Cd)	α(Cu)	α(Pb)	α(Zn)
α(Cd)	1			
α(Cu)	-0.63	1		
α(Pb)	-0.35	-0.21	1	
α(Zn)	0.11	0.47	-0.34	1
B				
α(Cd)	1			
α(Cu)	0.64	1		
α(Pb)	0.99	0.5	1	
α(Zn)	0.9	0.24	0.96	1
C				
α(Cd)	1			
α(Cu)	-1	1		
α(Pb)	1	-1	1	
α(Zn)	-1	1	-1	1

4.1.3.1.5 *Circle of correlation*

We next interpret the spatial structural correlation using principal component analysis. The application of correlation circle could give a direct impression of how the interrelations among different variables change at different spatial scales. Figure 4.4A shows the circle of correlation based on the original data of scale factors of heavy metals. Cu was clearly irrelevant to the first two principal components because of its small total variance (as mentioned in Section 4.1.3.1.2).

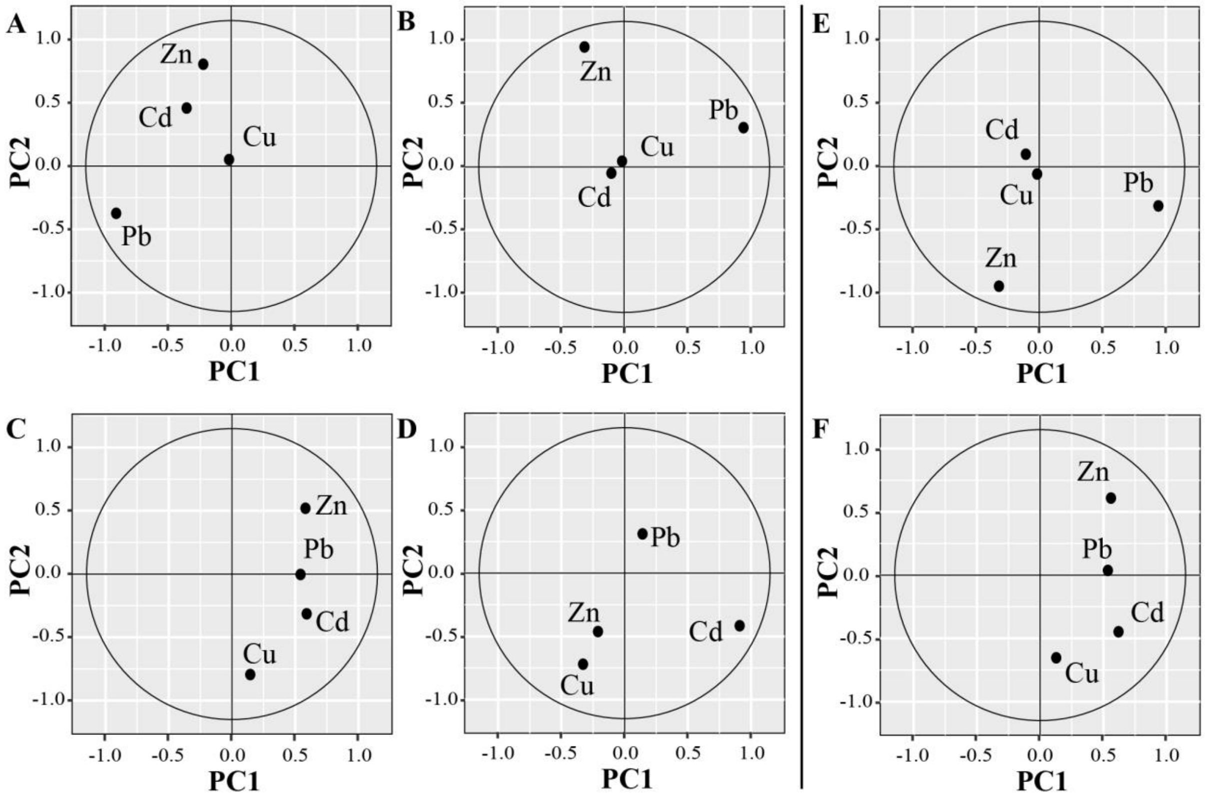

Figure 4. 4 Circles of correlation of Case Study 1 (Lathwehren) between scale factors of cadmium (Cd), zinc (Zn), copper (Cu), and lead (Pb), where data are from A: the general dataset, B: nugget scale, C: small scale with short range (24.6 m), D: large scale with long range (62.4 m), E: nugget scale after reducing one spatial structure, and F: small scale with a 23.6 m range after reducing one spatial structure. X axis: first principal component (PC1); Y axis: second principal component (PC2).

Pb was distinct from the others in the lower left quadrant and most relevant to the first principal component negatively. Cd and Zn were both in the upper left quadrant and together linked to the second principal component. At the nugget scale (Figure 4.4B), Pb and Zn were closely related to the first and the second principal components, respectively. Cd and Cu were irrelevantto the first two principal components. A distinct result at the small scale (Figure 4.4C) was that Cd, Zn, and Pb were significantly associated with the first principal component, which contrasts with Figure 4.4A. This clustering highlights the advantage of principal component analysis, as a large proportion of the spatial variances was captured at this scale. This analysis showed Cu to be distinct from the other three heavy metals. At the large scale (Figure 4.4D), the four heavy metals tended to be simultaneously correlated with first and second principal components but no association between the heavy metals was observed.

4.1.3.1.6 Single spherical model

Webster *et al.* (1994) suggested exploring the data pattern further by computing the leading principal components and plotting their variograms. As four variables are considered in the current study, two principal components should be sufficient to represent the principal features (Figure 4.5A). Figure 4.5B shows their histograms. The calculated components were then geostatistically analysed. The first and second principal components, however, showed no spatial structures (Figure 4.5C). This might explain the unusual relationship between coregionalized heavy metals at the large scale, since the variogram functions had become instable (Goovaerts, 1992).

As no spatial structures were evident in the principal components, we decided to reduce one spherical model on the linear model of coregionalization from the scale factors of sorption

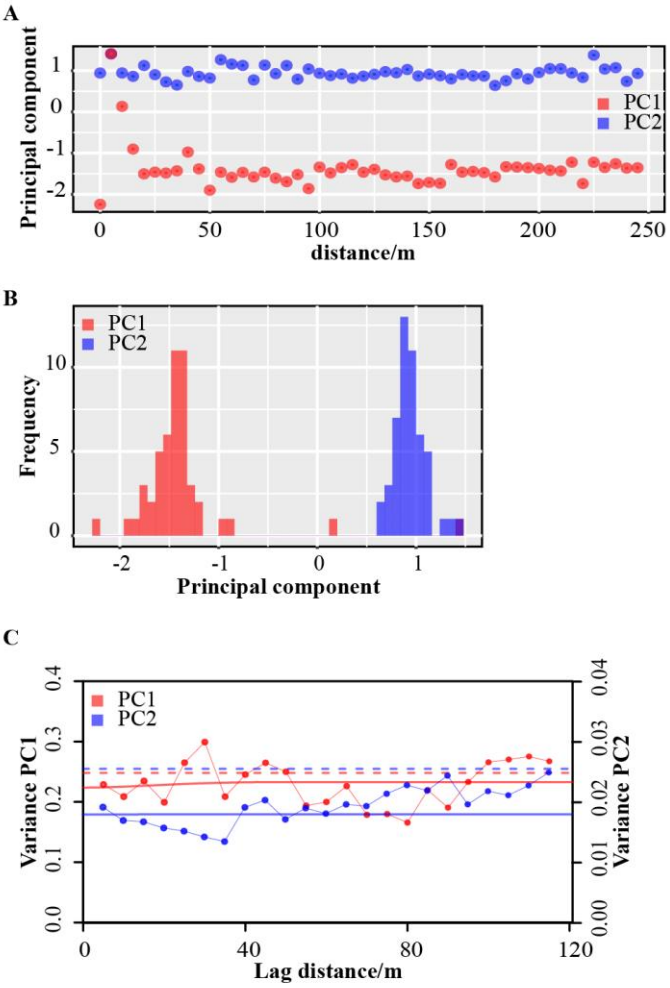

Figure 4. 5 Calculated first and second principal components (PC1 and PC2, respectively) of scale factors for four heavy metals (cadmium, zinc, copper, and lead) after principal component analysis. A: Spatial distribution along the 250-m transect, B: Histogram, and C: Variogram.

isotherms. After the reduction, their structural correlation coefficients (Table 4.3) were also determined. Significant correlations were observed at the small scale (Table 4.3B). The coefficient between Cd and Zn was enhanced from r = 0.5 to 0.8. Pb exhibited a significant correlation with both Cd and Zn at the small scale, where r = 0.94 and 0.95, respectively. The new circles of correlation at the nugget scale (Figure 4.4E) and the small scale (Figure 4.4F) were graphically similar as the coregionalized model with three spatial structures (Figure 4.4B–D), except for the up–down reversal in the position of the second principal component at the nugget scale. The reason that the reduction had no great impact on the results might be related to the relatively small variance represented at large scale (only 8% in Figure 4.1). We also noticed the same clustering between Cd, Zn, and Pb in Figure 4.4F as in Figure 4.4C. However, the auto-variogram of Pb indicates not a fairly good agreement at the small scale between the experimental points and the modelled ones (Figure 4.2). Nevertheless, the increased correlation of α_{iso} between Cd and Zn at the small scale, where the first principal component accounts for more than 87% of the total variance (Table 4.4), could be solid evidence indicating that the scale factors of sorption isotherms between Cd and Zn are spatially correlated.

Table 4. 3 A: nugget and B: structural correlation coefficients of Case Study 1 (Lathwehren) after reducing one spatial structure between scale factors of heavy metals.

A	α(Cd)	α(Cu)	α(Pb)	α(Zn)
α(Cd)	1			
α(Cu)	-0.77	1		
α(Pb)	-0.45	-0.16	1	
α(Zn)	0.06	0.42	-0.36	1
B				
α(Cd)	1			
α(Cu)	0.48	1		
α(Pb)	0.94	0.46	1	
α(Zn)	0.8	0.24	0.95	1

4.1.3.1.7 Spatial scale correlation between heavy metals and soil properties

As shown in Figure 4.1 and 4.3, the double-spherical coregionalisation model changed with the increasing number of variables. In order to eliminate the impact of internal coregionalisation,

Table 4. 4 Eigenvalues of correlation matrix at small scale of Case Study 1 (Lathwehren) after reducing one spatial structure.

Order	Eigenvalue	Proportion	Cumulative proportion
1	0.0284	87.28%	87.28%
2	0.0028	8.84%	96.12%
3	0.0012	3.88%	100%
4	0	0%	100%

the α_{iso} of the four heavy metals were then separately coregionalised with scaled physical-chemical soil properties, α_{sp}. The correlation circles are presented in Figure 4.6. The different background colours represent different data sources, which are original data (grey), data from nugget scale (red), data from small scale (green), and data from large scale (blue). In Figure 4.6A, Cd is located on the rightmost side of the abscissa axis, whereas other soil properties are distributed around the middle. Therefore, the variation of Cd, which is captured by the first principal component, had no common feature with other scaled soil properties. The same situation is shown in the circles of correlation at the nugget and small scales. In the long-range scale, the correlations appear as random scatter of the points. Increasing the number of variables also increased the spherical ranges, where the range of small scale became 57.5 m and the range of large scale was likewise increased from 62.4 to 86.25 m. The variation of Zn and Pb was the same as that of Cd either before or after decomposition (Figure 4.6B and 4.6D), and only one spherical structure was fitted by Pb. The first two principal components were not related to Cu in the original data (Figure 4.6C), while Cu had a relatively small total variance and a large correlation coefficient with the third principal component (data not shown). A significant correlation between Cu and clay content was found at the nugget scale (Figure 4.6C). However, as indicated in Figure 4.2, the variance of Cu at nugget scale represented a relatively small

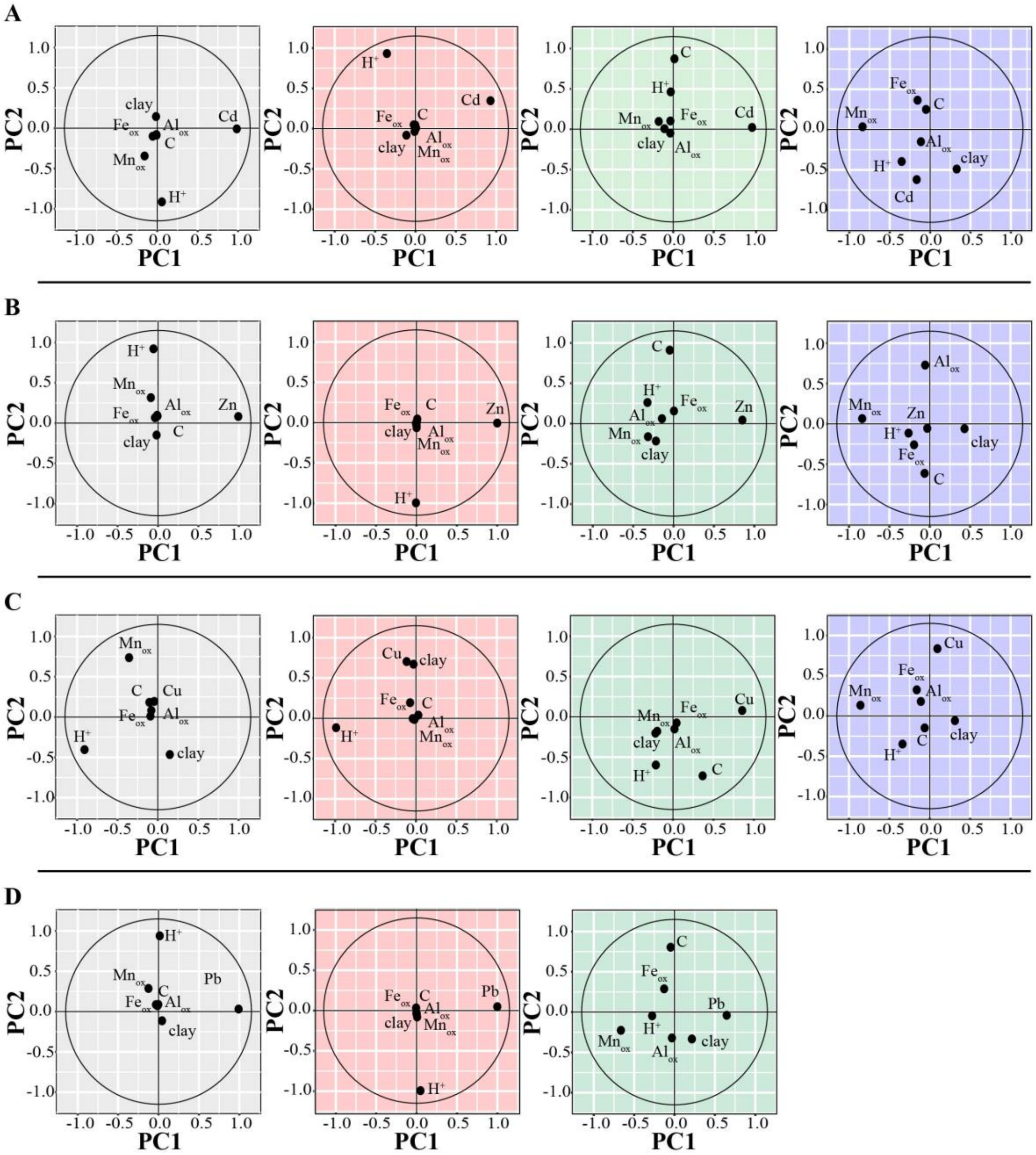

Figure 4. 6 Circles of correlation of Case Study 1 (Lathwehren) between the sorption property of heavy metals in soil and other relevant soil physico-chemical properties, where heavy metal is A: cadmium (Cd), B: zinc (Zn), C: copper (Cu), and D: lead (Pb). The plots with different background colours are based on different data, where grey represents data from the original sampling site, red represents data calculated at nugget scale, green represents data calculated at the small spatial scale, and blue represents data calculated at the large spatial scale. Note that the large-scale variance of Pb was reduced by fitting the variograms. X axis: first principal component (PC1); Y axis: second principal component (PC2).

proportion of total variance, which means that no effective relationship between the calculated scale factors from the sorption isotherms of the heavy metals and the corresponding soil properties was found.

4.1.3.2 Case study 2 (Vinnhorst dataset)

4.1.3.2.1 Results of decomposition

The soil of this case study was highly variable, as their texture crossed a broad range and showed a tendency from loam to sandy loam (Xiao *et al.*, 2015). The calculated correlation coefficients of α_{iso} between heavy metals themselves and α_{sp} of soil properties were also poorer than those in Case Study 1 (Table 4.1B). To eliminate the influence of this spatial tendency, a first-order differencing transformation based on a time series analysis in the previous study was performed. However, the correlation and uncertainty analysis demonstrated considerable difficulty in capturing the field-scale variability of sorption with suitable accuracy due to the unavoidable data transformation. In this study, a deterministic trend with spatially correlated random residuals from the trend instead of differencing was estimated by modelling the process. Among the different estimators, that of Oliver and Webster (2015) produced the optimal residual maximum likelihood for estimating the trend and the variogram parameters. After decomposition by the likelihood procedure, the original data were completely assigned into three parts, namely nugget effect, spatial variation, and horizontal trend (Figure 4.7). The trend parts were clearly different for the four heavy metals, where the downward tendency was much stronger for Zn and Pb than for Cd and Cu. It should be noted that the nugget parts of Zn and Pb were assigned with very small values (nearly zero) after fitting the program (data not shown).

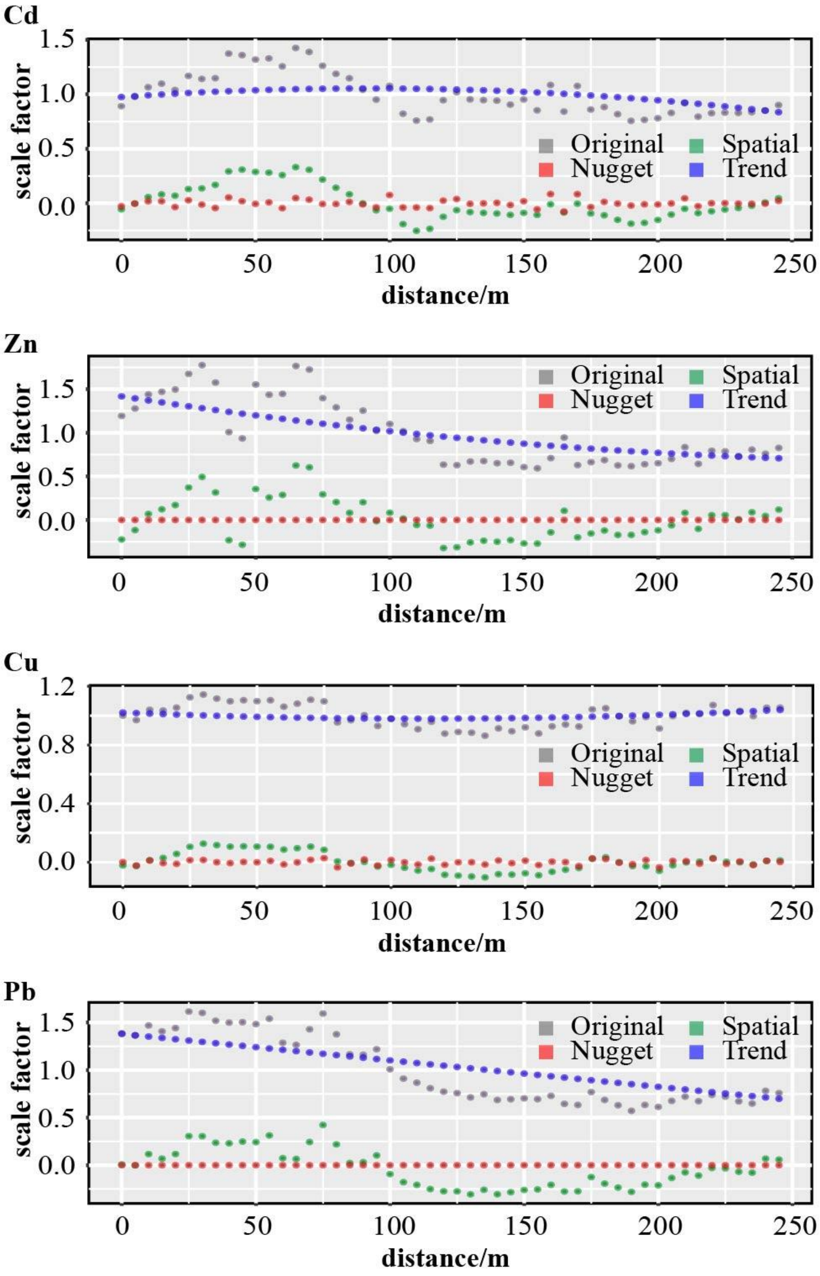

Figure 4. 7 General posting of scale factors of heavy metals between cadmium (Cd), zinc (Zn), copper (Cu), and lead (Pb) and their decompositions, namely nugget, spatial, and trend after residual maximum likelihood for a 250-m transect (50 samples) of the agricultural soils in Case Study 2 (Vinnhorst).

4.1.3.2.2 Circle of correlation

The results of principal component analysis performed on the α_{iso} data between heavy metals are given in Figure 4.8. Clearly, the correlation structure changed with original data and decomposed parts. Figure 4.8A shows the relationship of α_{iso} between the four heavy metals and the first two principal components based on the original data. Zn and Pb were mostly negatively related with the first principal component. Zn and Cd were the main contributors to the second principal component. At the nugget scale (Figure 4.8B), Zn and Pb were irrelevant to the first two principal components since they had only small values after calculation. Cd varied very differently to Cu, causing the first two principal components to actually be Cd and Cu themselves. At the spatial variation scale (Figure 4.8C), the position of the four heavy metals changed slightly compared with the original data (Figure 4.8A). Nonetheless, the result shows an association between Cd and Pb at this scale, which could not be recognised from the data before decomposition. At the trend scale (Figure 4.8D), Zn and Pb sharing the first principal component, owing to their relatively large horizontal trend. The trend of Cd varied very differently to the other three heavy metals and therefore it contributed to another principal component. Spatial-scale correlation between α_{iso} of heavy metals and α_{sp} of soil properties was also carried out and no relationship was observed (data not presented).

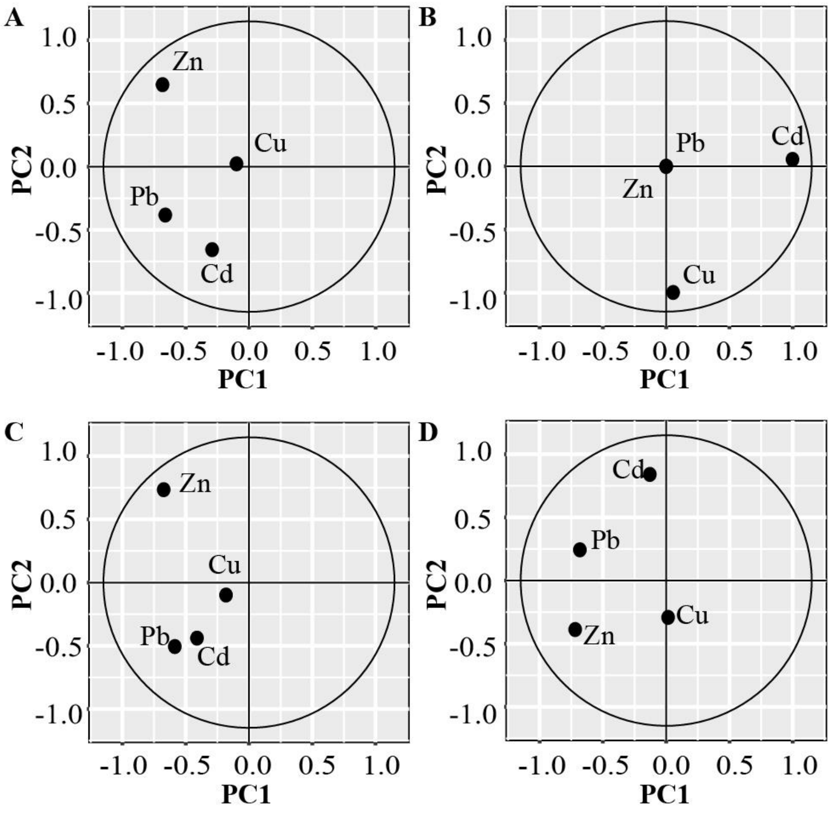

Figure 4. 8 Circles of correlation of Case Study 2 (Vinnhorst) between scale factors of cadmium (Cd), zinc (Zn), copper (Cu), and lead (Pb), where data are from A: the general dataset, B: calculated at nugget scale, C: calculated at spatial scale, and D: calculated at large scale treated as trend.

4.1.3.3 Discussion

The measurement of heavy metal sorption in soil is time consuming and much more difficult than measurement of other soil properties. The prediction of heavy metal sorption via pedotransfer function from the easily measurable soil properties is very common in soil science (Springob and Böttcher, 1998; Holm *et al.* 2003; Horn *et al.*, 2006; Altfelder *et al.* 2007). However, there is a clear disadvantage of these studies by quantification of the functional behaviour of a system, in which linear relationship between sorption isotherm parameters K and n was proven (Xiao *et al.*, 2015) and prediction based only on the variability of one key parameter may be incorrect and misleading (Böttcher, 1997). Therefore, determination of the scale factors of heavy metal sorption isotherms across a field could be a better alternative, which involves characterization of the spatial variability of heavy metal sorption behaviour in soil by functional normalization as only one single parameter. (Böttcher, 1997; Deurer and Böttcher, 2007; Xiao *et al.*, 2015).

In Case Study 1, we found the spatial dependence of α_{iso} of all heavy metals except Pb along the transect, which indicates that some variability could not be covered by the scale factors. In our previous study (Xiao *et al.*, 2015), we used reduction by scaling to quantify the efficiency of the scaling method. The smallest scaling reduction of sorption isotherms of Pb (64%) might explain why no spatial structure was found. Moreover, the variogram of native adsorbed Pb amount along the transect, S_0, revealed the same pure nugget structure (data not shown). The same spatial structures were also found by Streck and Richter (1997), who calculated the variograms of EDTA-extractable heavy metal contents in soil, where a spherical model of Cd with a range of 37 m and a nested model of Zn with ranges of 28 and 70 m, respectively, were fitted. Romano (2004) demonstrated a relatively good efficiency of a pedotransfer function in detecting the spatial dependency of a soil water retention variable, which also supports the potential usefulness of employing scaling to spatially quantify the sorption isotherms.

At the same time, we were aware that the semivariance of α_{iso} reached the upper bounds, where the total variance was already at small scale. Therefore, the instability observed at the large scale is reasonable and might be improved by the nested sampling strategy at the design step of the investigation. From the geostatistical perspective, Webster and Oliver (2007) also suggested nested survey and analysis as a first step in the description of variation in a previously little-known area with modest sampling effort. Moreover, the study of spatial multivariate correlation is not limited to three spatial structures; Wackernagel (1988) fitted 120 variograms from15 geochemical variables by using only two structures (one nugget and one spherical model).

From the circles of correlations between α_{iso} of heavy metals themselves and α_{sp} of soil properties, our results demonstrate that the spatial variation, i.e. the coefficients of variation, between coregionalized variables should be at least in the same order of magnitude (in Figure 4.9), otherwise even the scale-dependent analysis of the correlation structure among variables fails. In soil water research, Jury (1986) demonstrated that the rate parameters (e.g. hydraulic conductivity, sorption isotherm) are more spatially variable than the capacity parameters (e.g. bulk density, clay content) and require more intensive sampling density to determine an average or representative value.

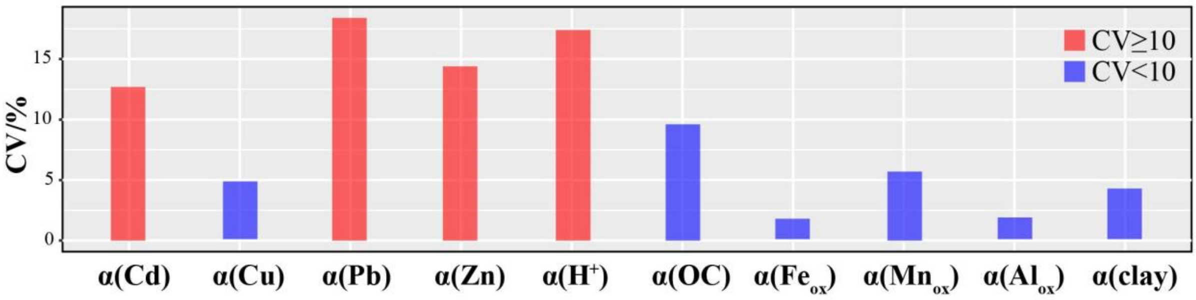

Figure 4. 9 Coefficients of variations (CV) of the scale factors in Case Study 1 (Lathwehren).

In the Case Study 2, residual maximum likelihood estimator was determined to separate the nonstationary in the mean. The detrending of scale factors for the sorption isotherms was successful, especially for Zn and Pb. We found a significant relationship between α_{iso} of Cd and Pb at the spatial variation scale, which was site- and scale-specific and was not generalisable. Moreover, we also noticed that either the linear mixed model or linear coregionalized model do not always meaningfully correspond to physical variables, since all these methods are purely mathematically calculated linear combinations of variables. How to make the analysis pedologically plausible remains an open question, since the complex variables arise from many processes and not all of these processes are well understood.

4.1.4 Conclusions

The spatial relationships between soil sorption properties among different heavy metals and soil physico-chemical properties by the means of scale factors were investigated using multivariate geostatistical analysis. The first objective was met by fitting the variograms of scale factors with one nugget scale and one small spherical scale. In Case Study 1, we found a principal component of small spatial scale, which was closely associated with the spatial correlation of sorption of two heavy metals. In contrast, we found no substantial spatial correlation between the sorption of heavy metals and other measured soil properties, indicating that the second objective was satisfied partially. There should be more pedological consideration when applying the detrending of residual maximum likelihood to make the data sufficiently reliable. Evidently, the demonstration of spatial correlation requires data in which the coefficients of variation do not differ too much. As a result, we conclude that further efforts are needed to theoretically develop the scaling relations of heavy metal sorption in soil, since the prediction of the behaviour of a particular natural phenomenon is never simple. The decomposition of spatial structures from soil sorption and relevant physico-chemical properties based on combining multivariate statistics and geostatistics is a powerful tool to reflect the principal features at different spatial scales. Once the scale-dependent correlation structure is determined, a geostatistical interpolation e.g. cokriging could be applied to reduce required number of samples and measurements or as guidance for a new sampling exercise in a cognate landscape.

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Chapter 5 Simulation of the Heavy Metal Transport

5.1 Simulation of the Heavy Metal Transport in Unsaturated Soils: Use of Scale Factors to Quantify Variable Sorption Isotherms

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Keywords: Scaling, sorption isotherm, heavy metal, transport.

Abstract

Heavy metals are toxic soil pollutants, which are retarded in soils by sorption at the solid phase. At a small scale (of a soil sample) the sorption process can be observed and quantified using sorption isotherms. However, most environmental problems have to be treated and solved at large scales (e.g., a field scale). At the field scale, heavy metal sorption isotherms are commonly highly variable in space. This spatial variability makes a representative quantification of the sorption process (e.g., for the soil protection or for the management of soil functions) and its consideration in reactive transport modelling (e.g., for groundwater protection) difficult. Many transport simulation studies therefore treat soils as homogeneous to avoid the need for complex datasets and calculations. In this study we used a recently developed method of scale sorption factors to quantify the spatial variability of heavy metal sorption in soils at the field scale. This method reduces the variability of sorption isotherms into a single average relation, while preserving their variation through the scale factors. We investigated the spatial variability of heavy metal sorption isotherms for an agricultural field on a Luvisol developed over a loess material near Hannover, Germany. Fifty samples were taken from A and B horizons along a 250-m transect. Sorption isotherms for heavy metals and soil properties, such as pH, CEC, and texture, were measured and scale factors were calculated. The heavy metal transport was simulated with the HYDRUS model using a unique reference sorption isotherm (derived using the scale procedure or mixed soil samples). Spatial variability of sorption at every sampling point was further represented using a scale factor, which was either directly calculated (using a scaling procedure) or indirectly estimated (using regression models with another heavy metal or from soil properties). And for comparison variability of sorption was also simulated using the original measured Freundlich parameters.

The results show that scale factors are well applicable to predict spatially variable retardation and transport of heavy metals in soil, although a certain reduction of variability is to be expected. In case of extreme situations transport simulations with scale factors are not well suited to describe the depth distribution of heavy metal concentrations, especially when using indirectly calculated scale factors.

5.1.1 Introduction

Both agricultural (He *et al.*, 2005; Nicholson, 2003) and environmental (Bradl, 2005) sciences treat heavy metals as an important environmental factor because of their negative impact on the ecosystem. Soils are contaminated by heavy metals either gradually due to their long-term depositions or suddenly due to various industrial leaks or intentional applications of various compounds (e.g., sewage sludge, manure). The fate and transport of heavy metals in soils depend mainly on their reactive properties, with sorption reactions being the most important ones (Alloway, 1995). The soil can then act as a storage container for these contaminants. A lot of studies reported spatial distributions of heavy metals in the subsurface (Yang, 1989; Camobreco, 1996; Ingwersen *et al.*, 2006). However, much attention has been paid to transport processes in one-dimensional soil columns, without extending the transport into two or three dimensions. Soil spatial heterogeneity, which makes the sorption highly variable, is the main reason for the lack of extending transport studies into higher dimensions.

Sorption processes cause the retardation of heavy metals in soils (Sparks, 2003). Hence, the quantification of sorption isotherms and their spatial variability is a prerequisite to quantify the spatial variability of heavy metal transport in in soils. To simulate heavy metal displacement at the field scale Streck *et al.* (1997) used a parallel soil column approach. Altfelder *et al.* (2007) have studied the combination of uncertainty and variability to predict field-scale heavy metal transport. The authors have quantified sorption isotherms through pedotransfer functions (PTF). Deurer and Boettcher (2007) have compared PTF and a scaling method for sorption isotherms (Böttcher, 1997) to upscale the small scale transport variability and concluded that mean sorption behaviour derived through scaling resulted in smaller uncertainty of heavy metal transport prognoses.

Scaling was used first in soil hydrology to quantify the variation of water retention (Miller and Miller, 1956, Russo and Bresler, 1980; Raats *et al.*, 2006). Following the basic ideas and rules of scaling (Tillotson and Nielsen, 1984) Böttcher (1997) has developed a method to calculate scale factors for spatially variable sorption isotherms, and successfully applied this method to Cd sorption in sandy soil. Furthermore, Böttcher (1997) showed that the scale factors for sorption isotherms were correlated with some soil physicochemical properties. Therefore, indirect calculation of scale factors for sorption from physicochemical soil properties (indirect scaling procedure) seems possible. If so, scale factors may be derived by direct or indirect procedures. This would extend the use of scale factors from statistical description of spatially variable sorption isotherms (direct scaling procedure) to broadened application in prediction of reactive transport processes in soil by the indirect scaling procedure.

In this study, scenarios of heavy metal (Cadmium, Zinc and Copper) transport in unsaturated soil using the direct and indirect scaling procedure were simulated with HYDRUS 2D. The main objective was to prove the performance of the two scaling procedures in simulating spatially variable heavy metal transport compared to simulations with original sorption data.

5.1.2 Material and Methods

5.1.2.1 Soil samples

The soil samples (undisturbed and disturbed) were taken from an agricultural field on a Luvisol developed in loess material near Hannover, Germany. Each 50 samples were taken along a 250 m transect at every five meter from 0 to 30 cm (topsoil) and 30 to 60 cm (subsoil). For each horizon one mixed sample was made from the 50 soil samples to measure a mean sorption isotherm that is needed as reference in the indirect scaling procedure (see 5.1.2.4).

5.1.2.2 Laboratory analyses

The undisturbed soil samples were used to measure the bulk density and water content. The disturbed soil samples were air dried and sieved. Then the samples were used to measure the relevant soil physicochemical properties (Table 5.1).

Sorption isotherms were measured in batch experiment. Heavy metal solutions (concentration ranges from 0 to 20 mg/L Cadmium, 75 mg/L Zinc and 40 mg/L Copper) were added to the soil water suspensions. $Ca(NO_3)_2$ electrolyte solution was also added to maintain the natural ionic strength. After 24h shaking end over the suspensions were centrifuged for 15 minutes. Then heavy metal concentrations were measured in the supernatant by ICP-OES.

Table 5. 1 Methods for measuring physico-chemical soil properties. (Source: Utermann *et al.*, 2005)

Soil property [Unit]	Method
Texture [%]	Pipette method after Koehn (<63 µm) Dry sieving (>63 µm) DIN* 19683-2
pH ($CaCl_2$) [-]	Potentiometric by use of a glass electrode in 0.001 M $CaCl_2$ DIN ISO^ 10390:1997
Total carbon [%]	C-N-S elementary analysis DIN ISO 10694
Total carbonate [%]	Gas volumetric DIN ISO 10693 (1997)
Total organic carbon (OC) [%]	Difference between total carbon and total carbonate
Oxalate extractable oxide by Fe, Mn and Al (Fe_{ox}, Mn_{ox}, Al_{ox}) [mg kg^{-1}]	Extraction with oxalic acid ammonium oxalate DIN 19684-6 Measure with flame-AAS
Effective cation exchange capacity (CEC_{eff}) [$mmol_c$ kg^{-1}]	Percolation with 0.1 M $BaCl_2$ Modified by DIN 19684-8 Measurement of Ca, Mg, K, Na, Fe, Mn and Al with ICP-OES, determination of H^+ ion concentrations from pH value

* German Institute for Standardization

^ International Organization for Standardization

5.1.2.3 Parameterization of heavy metal sorption isotherm

From measured sorption data sorption isotherms were calculated, and the Freundlich equation (Bradl, 2005) was used to describe the isotherms.

$$\mathrm{S} = \mathrm{K} \times C^{n} \tag{5.1}$$

In the Freundlich equation, *S* is the sorbed fraction [μg/kg], *C* is the solution concentration [μg/L], and *K* and *n* are parameters, adjusted by fitting the equation to the measured data.

5.1.2.4 Scaling of sorption isotherms

The scaling rule for direct scaling of sorption isotherms derived by Böttcher (1997) is:

$$C^{*} = \alpha^{2} C_{i} \tag{5.2}$$

where C^* is the scaled concentration, C_i is a measured concentration, and α is the scale factor.

5.1.2.5 Direct Scaling Procedure

In the direct scaling procedure, firstly mean concentrations describing the reference isotherm are derived as scale means (Böttcher, 1997) from

$$M_{r,j} = R^{2}\left[\sum_{r=1}^{R}\left(\sqrt{C_{r,j}}\right)^{-1}\right]^{-2} \tag{5.3}$$

Secondly, scale factors are calculated under the constraint

$$\sum_{r=1}^{R} \alpha_r R^{-1} = 1 \tag{5.4}$$

by minimization of the sum of squares (in logarithmic space)

$$SS = \sum_{r=1}^{R} \sum_{j=1}^{J} \left(lnM_{r,j} - 2ln\alpha_r - lnC_{r,j} \right)^2 \tag{5.5}$$

to obtain α as:

$$\alpha = exp\left[(2J_r)^{-1} \sum_{j=1}^{J_r} \left(ln\, M_{r,j} - ln\, C_{r,j} \right) \right] \tag{5.6}$$

In the equations r is the number of soil samples (R = maxima) and j is the number of data points on the respective sorption isotherm (J = maxima). C represents the individual measured concentration and M is the scale mean concentration.

The ratio (SS_{before}-SS_{after})/SS_{before} is used to quantify the scaling efficiency. More details are given in Böttcher (1997).

5.1.2.6 *Indirect Scaling Procedure*

Not only scale factors for sorption isotherms but also scale factors for soil properties were calculated based on principles outlined in Tillotson and Nielsen (1984). And using correlations between heahy metal sorption and soil properties an indirect scaling procedure was developed.

The concept of indirect scaling is based on the assumption, that the measured sorption isotherm of mixed samples is comparable with the mean sorption isotherm derived from direct scaling procedure, and scale factors can be calculated from scale factors of sorption relevant soil properties using multiple linear regression:

$$\alpha_{in} = \alpha^{*} + a\alpha_{pH} + b\alpha_{clay} + c\alpha_{OC} + \cdots \tag{5.7}$$

where α_{in} is scale factor of indirect scaling and α^{*} is intrinsic scale factor, α_{pH}, α_{clay} and α_{OC} are calculated scale factors of soil properties, and a, b and c are fitting parameters of linear regression.

5.1.2.7 Simulation of heavy metal transport with HYDRUS

In unsaturated soil the water flow is usually vertical. Hence, the simultaneous heavy metal transport is also vertical and can be described by the widely used convection-dispersion equation (CDE) under steady flow conditions (Radcliffe and Šimůnek, 2010).

As the sampling was along a transect at every 5 m, the geometry in HYDRUS was set as a rectangle, which has a length of 250 m and a depth of 0.6 m. The rectangles were divided into 50 columns each with topsoil and subsoil horizon. Each column has a single set of water flow and solute transport parameters. The infiltration rate was 250 mm per year (Deurer and Böttcher, 2007). The input concentrations were set to 100 µg/L for Cd, 8000 µg/L for Zn and 2000 µg/L for Cu. The simulations time was set to 500 years for Cd and Zn, and 100 years for Cu.

Three scenarios were set up. Scenario I was simulated using the original measured sorption parameters. In scenario II the reference isotherms (Table 3) for the soil horizons were used, and the scale factors from the direct scaling procedure were applied to calculate the sorption isotherms for the soil columns. In the scenario III the sorption isotherms for the columns were calculated from the isotherm of the mixed soil sample and the scale factors from the indirect scaling procedure.

5.1.3 Results and Discussion

5.1.3.1 *Sorption isotherm parameters and physico-chemical soil properties*

Table 5.2 lists the mean and the coefficient of variation (CV) of the measured soil properties and the Freundlich parameters. Differences between soil properties in topsoil and subsoil are low. pH values are high, causing strong heavy metal sorption in topsoil and subsoil. The sorption parameter *K* of Cd and Zn in subsoil is much higher than in topsoil, possibly because of higher *pH* in subsoil, though n is more or less the same. *K* and *n* of Cu behave different, which may be attributed to the higher *OC* content in the topsoil. Most CVs in Tab. 5.2 are low, except CV of CEC_{eff} and *K*. This finding hints at correlation between *CEC* and *K* as already published by others (e.g. Buchter *et al.*, 1989, Springob and Böttcher, 1998).

5.1.3.2 *Reference isotherm and scale factors*

A summary of sorption isotherm parameters, scale factors from direct and indirect scaling procedure, and their statistics is presented in Table 5.3. Because the mean of scale factors is always 1 (compare to eq. 5.4), the range of scale factors with coefficient of variation is given. CVs of scale factors α appear to be lower than CVs of *K* in table 5.2 and higher than CVs of *n* in consideration of residual sum of squares. As shown in table 5.3 the scaling efficiencies (derived for direct scaling) are mostly high. This confirms earlier findings of Böttcher (1997) and Deurer and Böttcher (2007) who showed for sandy soils that successful scaling of sorption isotherms is possible.

The values of Adj. R^2 for indirect scale factors are low indicating only weak correlation between measured soil properties and scale factors. The reason could be various, inter alia, such as relative small sample size and low CVs of soil properties. The reference sorption isotherms of direct scaling procedure fit quiet well with sorption isotherms of indirect scaling procedure (measured from mixed soil samples). This demonstrates that scale means are meaningful estimators to upscale soil sorption properties from point measurements to the field scale.

5.1.3.3 Evaluation of heavy metal transport

The simulated heavy metal concentrations are shown in Figure 5.1. The spatial variation of concentration depth distributions along the transect between the different simulation scenarios is basically the same for each heavy metal. However, the extend of transport variability is in the order Scenario I > II > III. These results indicate that application of scale factors for sorption isotherms, especially indirect scale factors, cause a certain reduction of the variability of heavy metal retardation in soil, while the typical transport behaviour of the metals is maintained.

Unlike Cd and Cu, Zn shows an almost very good match between model results simulated with the original topsoil sorption data or scale factors, respectively, regardless of the scaling procedure. This is very probably due to two reasons. First, Zn topsoil has a scaling efficiency of 88% (Table 5.3), which is higher than for Cd (85%) and Cu (78%). Second, Zn topsoil has low CVs of sorption isotherm parameters K (CV=24%) and n (CV=5%). Compared to Cd and Cu these values are closer to the CVs of α and αin (Table 5.3). Also Nanos and Martín (2012) found that Zn concentrations in soil are spatially not as variable as Cd and Cu concentrations. On the other hand the simulation scenarios for the spatially highly variable heavy metal Cu demonstrate a disadvantage of sorption scale factors. Only at column 13 (from the left of the

Table 5. 2 Summary statistics of soil properties and isotherm parameters.

		pH	CEC_{eff}	OC	sand	clay	silt	Fe_{ox}	Al_{ox}	Mn_{ox}	K n (Cd)	K n (Zn)	K n (Cu)
		-	$\frac{mmol}{kg}$	%	%	%	%	$\frac{mg}{kg}$	$\frac{mg}{kg}$	$\frac{mg}{kg}$	[]^	[]	[]
Mean	Topsoil	6.9	96.8	1.18	3.8	11	85	2617	581	356	1407 0.81	7498 0.51	247 1.34
	Subsoil	7.2	72.9	0.31	3.3	12	85	2621	603	228	2271 0.80	13509 0.49	123 1.66
		%	%	%	%	%	%	%	%	%	%	%	%
CV*	Topsoil	2	40	10	9	1	12	4	4	10	34 7	24 5	34 6
	Subsoil	2	42	17	13	2	10	5	6	17	33 6	17 7	49 9

Table 5. 3 Scale factors and reference isotherms from direct and indirect scaling procedure, and statistical parameters.

Heavy metal	Horizon	Sample size	Direct scaling procedure			Indirect scaling procedure		
			α Range [-] CV [%]	R-SI*	SE^ %	α_{in} Range [-] CV [%]	Adj. R^2	SI_{mixed}#
Cd	topsoil	50	0.67 13	$S=1394C^{0.80}$	85	0.51 10	0.513	$S=1398C^{0.83}$
	subsoil	50	0.87 16	$S=2248C^{0.79}$	92	0.42 13	0.503	$S=2229C^{0.77}$
Zn	topsoil	50	0.71 14	$S=7482C^{0.51}$	88	0.55 11	0.505	$S=8709C^{0.49}$
	subsoil	50	0.81 14	$S=13638C^{0.49}$	75	0.29 7	0.248	$S=15612C^{0.44}$
Cu	topsoil	50	0.23 5	$S=245C^{1.33}$	78	0.13 3	0.443	$S=275C^{1.30}$
	subsoil	50	0.39 10	$S=118C^{1.64}$	89	0.32 8	0.612	$S=161C^{1.59}$

* Reference sorption isotherm

^ Scaling efficiency

Sorption isotherm derived from mixed sample

transect, Fig. 5.1) the maximum Cu concentration has already been transported to a depth >60 cm if simulated with the original sorption data (Scenario I). If simulated with direct scale factors (Scenario II) or indirect scale factors (Scenario III), respectively, only a slightly deeper or rather similar depth transport of Cu in column 13 is visible, compared to the columns in the surrounding (Fig. 5.1).

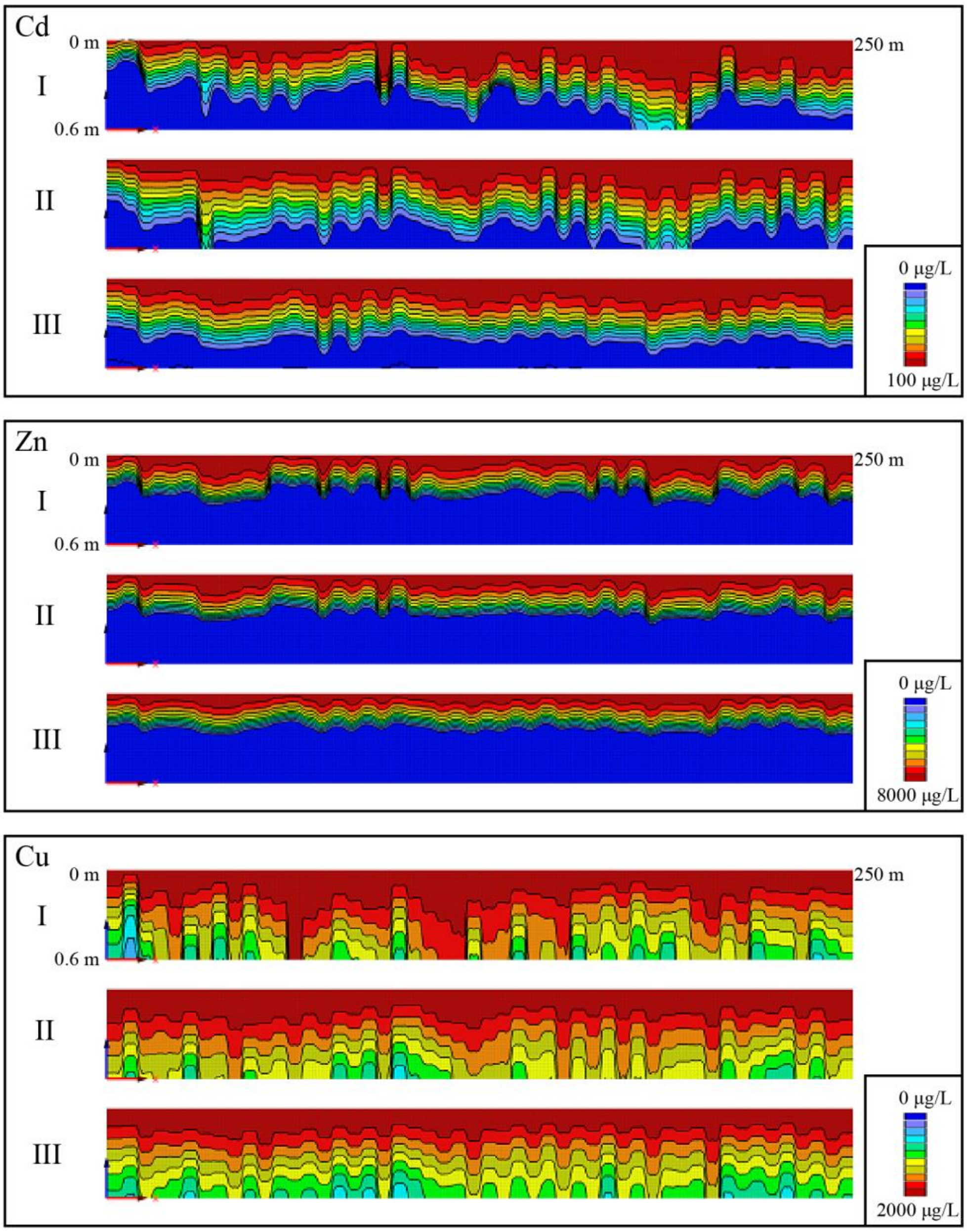

Figure 5. 1 The simulation scenarios of heavy metal transport with I: original sorption procedure, II: direct scaling procedure, III: indirect scaling procedure.

The reason for this behaviour may be explained by comparing Freundlich parameters *K* and scale factors. The original Freundlich *K* at column 13 is 98.7 µg$^{1\text{-}n}$L^n/kg. Obviously, Cu retardation at this point (column 13) is extremely week. In the contrast, the mean *K* of directly calculated reference isotherm and *K* of mixed sample are 244.8 µg$^{1\text{-}n}$L^n/kg and 274.8 µg$^{1\text{-}n}$L^n/kg, respectively. I.e., the ratios are 0.4 and 0.36, respectively. But the corresponding squared scale factors α^2 (eq. 5.2) are 0.82 and 0.91. Thus, by scale factors a much stronger retardation of Cu is simulated at column 13. This shows that scale factors, and especially scale factors of the applied indirect scaling procedure (uncertain as indicated by low Adj. R^2, Tab. 5.3), are not well suited to describe extreme situations at single points in space.

Summarized, the simulated scenarios show that scale factors are applicable to predict spatially variable retardation and transport of heavy metals in soil, although a certain reduction of variability is to be expected. In case of extreme situations transport simulations with scale factors are not well suited to describe the depth distribution of heavy metal concentrations.

5.1.4 Conclusions

We demonstrated that the calculation of scale factors is a convenient and effective method (due to high scaling efficiency) to derive the mean sorption isotherm at field scale. We conclude that scale factors have the potential to describe the spatial variability of heavy metal transport well, if the variability of sorption isotherms is not too high, as it is e.g. in case of Zn. In extreme situations (very week heavy metal sorption) at single points scale factors may be not sufficiently effective to simulate sorption or retardation, respectively. In such a case especially the indirect scaling procedure fails because of the high uncertainty of the multiple regression. But also in general the applied indirect scaling procedure tends to level out the variability of heavy metal transport, and thus cannot be recommended as an effective tool for heavy metal transport prediction. Further studies should concentrate on developing an improved indirect scaling procedure, possibly including other sorption relevant soil properties as e.g. specific soil surface area.

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Chapter 6 Final Discussion

The aim of this dissertation is to quantify the relationship between the sorption isotherms of heavy metals themselves and the attendant physico- chemical soil properties by condensation their field scale variability into scale factors. Accordingly, functional normalization under Böttcher's scaling rule has been applied to the measured soil sorption isotherms (cadmium, copper, lead and zinc) and other soil properties, targeting a representative simplification of soil information from loess soil at Lathwehren site near the city of Hannover, Germany and loamy to sandy soil at Vinnhorst site in Hannover, respectively (*Chapter 2 and 3*). Field-scale variability of heavy metal sorption isotherms was explored by Pearson product-moment correlation with soil properties, where scaling was used to simplify the description of the statistical variations in the sorption properties at the field scale (*Chapter 3*). Using the multivariate geostatistical analysis and residual maximum likelihood, furthermore, the spatial structural correlation among heavy metals sorption and soil properties have been systematically examined (*Chapter 4*). Coupled with HYDRUS 2D, scenarios of heavy metal (cadmium, zinc and copper) transport in unsaturated soil using the direct and indirect scaling procedure have been illustrated (*Chapter 5*), and some suggestions of scaling theory were given.

The most attractive feature of scaling is the ability, which potentially reduces the wide spread of the sorption isotherms into an average isotherm, but preserves the variation through calculated scale factors. For that reason, two study sites (Lathwehren with loess soil, Vinnhorst with loamy to sandy soil) were chosen near the city of Hannover, Germany. Along a 250 m transect, 50 samples were taken at two depths for each site. Sorption isotherms of cadmium, copper, zinc and lead were measured, along with a range of soil properties, including pH, cation exchange capacity, organic carbon content, and texture. The isotherms were profitably parameterized by the Freundlich equation and were showed a large spatial variability.

Calculation of scale factors was primarily carried out for all the following studies. The correlations were tested between scale factors of different heavy metal sorption isotherms, and also to soil properties. Site- and depth specific relationships between scale factors of heavy metal sorption isotherms were found. Moreover, significant correlations between scale factors of heavy metal sorption isotherms and soil properties occurred only sporadically. Based on these sporadic and not transferrable correlations, e.g. with organic carbon content and cation exchange capacity, a moderate prediction of the field-scale variability of copper sorption was made after the regression analysis for the Lathwehren subsoil. Last but not least, proving whether the average isotherms can be represented by a single measured isotherm of the composite samples from the area was also an objective. This was found to hold at the loess soil, but not at the loamy to sandy soil, which indicates that scaling is favorable to homogeneous sites.

These results brought up the new question, whether the relationship between heavy metals' sorption and soil properties in a field scale could be improved. The spatial structural relationships of scale factors for the sorption isotherms between different heavy metal species and scale factors of soil properties were then analyzed by linear model of coregionalization and principal component analysis according to the potential correlations at different scales. By the loess site, the variogram of heavy metal's sorption was fitted by three spatial structures, i.e. one nugget and two spherical scales. Unfortunately, the correlation between heavy metals was unusual at large scale and then only two spatial structures were left. Despite it, the circles of correlation revealed distinguishing results from ordinary relationships, where we found a principal component of small spatial scale that was associated tightly to the spatial correlation of two heavy metals' sorption. The scaled soil physico-chemical properties were, however, not correlated with scale factors of heavy metal sorption isotherms at each nested scale. At the site of Vinnhorst, presented nonstationary in the mean, the data were transformed by residual maximum likelihood and the sorption of lead in soil was found correlated to the one of cadmium at the spatial variation scale.

Further, an approach to simulate the heavy metal transport was done by using a unique reference sorption isotherm (derived using the scale procedure or a single measured isotherm of the composite samples). Spatial variability of sorption at every sampling point was in addition represented applying a scale factor, which was either directly calculated (using a scaling procedure) or indirectly estimated (using regression models with another heavy metal or from soil properties). For comparison, variability of sorption was also simulated using the original measured Freundlich parameters. The results showed that scale factors are well applicable to predict spatially variable retardation and transport of heavy metals in soil, although a certain reduction of variability is to be expected. In case of extreme situations, transport simulations with scale factors were not well suited to describe the depth distribution of heavy metal concentrations, especially when using indirectly calculated scale factors.

In summary, it is worth to quantify and express field-scale variability of heavy metal sorption isotherms in soils by using scaling. However, the complexity of heavy metal’s sorption in soil makes the analysis at state of the art not be able to describe it completely. Low reduction of scaling, e.g. Pb at Lathwehren, and nonstationary in the mean at Vinnhorst made the fitting of variograms problematic. Besides, the sampling campaigns for evaluation of sorption variability should consider 80 to 100 samples per site, which are obviously greater than the original 50 samples. All of these illustrated problems limited the application of scale factors for heavy metal sorption isotherms, which can only be performed at specific case studies or scenario modeling. The further work on scaling is to conduct a thorough improvement of the original theory of scaling by modifying its underlying assumptions, the algebra of scaling methods, and the feasibility of using scaling to enrich and advance the study of heavy metal sorption at the field scale in the future.

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