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

Han Xiao¹, Jürgen Böttcher², and Jiří Šimůnek³

¹Institute of Soil Science, Leibniz University of Hannover, Hannover, Germany, xiao@ifbk.uni-hannover.de
²Institute of Soil Science, Leibniz University of Hannover, Hannover, Germany, boettcher@ifbk.uni-hannover.de
³Department of Environmental Sciences, University of California, Riverside, CA 92521, USA, jiri.simunek@ucr.edu

Abstract

Heavy metals are toxic soil pollutants that 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). For comparison, variability of sorption was also simulated using the original, measured Freundlich parameters.

The results show that scale factors are well suited for predicting spatially variable retardation and transport of heavy metals in soil, although a certain reduction of variability is to be expected. In the 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.

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 either gradually contaminated by heavy metals 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 depends 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 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. These authors have quantified sorption isotherms through pedotransfer functions (PTF). Deurer and Boettcher (2007) have studied the combination of uncertainty and variability to predict field-scale heavy metal transport. These authors have quantified sorption isotherms through pedotransfer functions (PTF). Deurer and Boettcher (2007) have compared PTF and a scaling method for sorption isotherms (Boettcher, 1997) to upscale the small scale transport variability and concluded that mean sorption behavior 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 a broadened application in the 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 (Šimůnek et al., 2011). 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.

2. Material and Methods

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. 50 samples were taken along a 250 m transect at every five meters 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 a reference in the indirect scaling procedure (see 2.4.2).
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 1).

Table 1. Soil physicochemical properties used to quantify the scale factors and the measurements method (source: Utermann et al., 2005).

<table>
<thead>
<tr>
<th>Soil property [Unit]</th>
<th>Method</th>
</tr>
</thead>
</table>
| Texture [%] | Pipette method after Koehn (<63µm)  
Dry sieving (>63µm)  
DIN¹ 19683-2 |
| pH(CaCl\textsubscript{2}) [-] | Potentiometric by use of a glass electrode in 0.001 M CaCl\textsubscript{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\textsubscript{ox}, Mn\textsubscript{ox}, Al\textsubscript{ox}) [mg/kg] | Extraction with oxalic acid ammonium oxalate  
DIN 19684-6  
Measure with flame-AAS |
| Effective cation exchange capacity (CEC\textsubscript{eff}) [mmol/kg] | Percolation with 0.1 M BaCl\textsubscript{2}  
Modified by DIN 19684-8  
Measure of Ca, Mg, K, Na, Fe, Mn and Al with ICP-OES, determination of H\textsuperscript{+}-ions-concentration from pH-Value |

¹German Institute for Standardization  
^International Organization for Standardization

Sorption isotherms were measured in a batch experiment. Heavy metal solutions (concentrations range from 0 to 20 mg/L for Cadmium, 75 mg/L for Zinc and 40 mg/L for Copper) were added to the soil water suspensions. A Ca(NO\textsubscript{3})\textsubscript{2} electrolyte solution was also added to maintain the natural ionic strength. After 24 h of shaking, the suspensions were centrifuged for 15 minutes. Heavy metal concentrations were then measured in the supernatant by ICP-OES.

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.

\[ S = K \cdot C^n \]  
\[(1)\]

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.

2.4. *Scaling of Sorption Isotherms*

The scaling rule of sorption isotherms derived by Böttcher (1997) is:
\[ C^* = \alpha^2 C_i \]  

(2)  

where \( C^* \) is the scaled concentration, \( C_i \) is a measured concentration, and \( \alpha \) is the scale factor.

2.4.1 Direct Scaling Procedure

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

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

(1)

Second, scale factors are calculated under the constraint

\[ \sum_{r=1}^{R} a_r R^{-1} = 1 \]  

(2)

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

\[ SS = \sum_{r=1}^{R} \sum_{j=1}^{J} \left( \ln M_{r,j} - 2 \ln a_r - \ln C_{r,j} \right)^2 \]  

(3)

to obtain \( \alpha \) as:

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

(6)

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

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

2.4.2 Indirect Scaling Procedure

Both scale factors for sorption isotherms and scale factors for soil properties were calculated based on principles outlined in Tillotson and Nielsen (1984). Using correlations between heavy metal sorption and soil properties, an indirect scaling procedure was also 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 the direct scaling
procedure, and that scale factors can be calculated from scale factors from soil properties relevant to sorption using multiple linear regression:

\[ \alpha_{in} = \alpha^* + a\alpha_{pH} + b\alpha_{clay} + c\alpha_{OC} + \ldots \]  

(7)

where \( \alpha_{in} \) is the scale factor of indirect scaling and \( \alpha^* \) is an intrinsic scale factor, \( \alpha_{pH} \), \( \alpha_{clay} \) and \( \alpha_{OC} \) are calculated scale factors of soil properties, and \( a \), \( b \), and \( c \) are fitting parameters of linear regression.

2.5. 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 sampling was carried out along a transect at every 5 m, the geometry in HYDRUS-2D was set as a rectangle with a length of 250 m and a depth of 0.6 m. The rectangles were divided into 50 columns, each with topsoil and subsoil horizons. Each column has a single set of water flow and solute transport parameters. The infiltration rate was 250 mm per year (Deurer, 2007). The input concentrations were set to 100 for Cd, 8000 for Zn, and 2000 μg/L for Cu. The simulation 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 scenario III, sorption isotherms for the columns were calculated from the isotherm of the mixed soil sample, and the scale factors from the indirect scaling procedure.

3. Results

3.1. Sorption Isotherm Parameters and Physicochemical Soil Properties

Table 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. The 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 a higher pH in the subsoil, though \( n \) is more or less the same. \( K \) and \( n \) of Cu behave differently, which may be attributed to the higher OC content in the topsoil. Most CVs in Tab. 2 are low, except the CV of \( CEC_{eff} \) and \( K \). This finding hints at a correlation between \( CEC \) and \( K \), as already published by others (e.g., Buchter et al., 1989, Springob and Böttcher, 1998).
Table 2. Summary statistics of soil properties and isotherm parameters.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>CEC&lt;sub&gt;eff&lt;/sub&gt;</th>
<th>OC</th>
<th>sand</th>
<th>clay</th>
<th>silt</th>
<th>Fe&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>Mn&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>K&lt;sub&gt;n&lt;/sub&gt; (Cd)</th>
<th>K&lt;sub&gt;n&lt;/sub&gt; (Zn)</th>
<th>K&lt;sub&gt;n&lt;/sub&gt; (Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mmol&lt;sub&gt;kg&lt;/sub&gt;</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>mg&lt;sub&gt;kg&lt;/sub&gt;</td>
<td>mg&lt;sub&gt;kg&lt;/sub&gt;</td>
<td>mg&lt;sub&gt;kg&lt;/sub&gt;</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
</tr>
<tr>
<td>Mean Topsoil</td>
<td>6.9</td>
<td>96.8</td>
<td>1.18</td>
<td>3.8</td>
<td>11</td>
<td>85</td>
<td>2617</td>
<td>581</td>
<td>356</td>
<td>1407.0±0.81</td>
<td>7498.0±0.51</td>
<td>247.1±1.34</td>
</tr>
<tr>
<td>Mean Subsoil</td>
<td>7.2</td>
<td>72.9</td>
<td>0.31</td>
<td>3.3</td>
<td>12</td>
<td>85</td>
<td>2621</td>
<td>603</td>
<td>228</td>
<td>2271.0±0.80</td>
<td>13509.0±0.49</td>
<td>123.1±1.66</td>
</tr>
<tr>
<td>CV&lt;sup&gt;+&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Topsoil</td>
<td>2</td>
<td>40</td>
<td>10</td>
<td>9</td>
<td>1</td>
<td>12</td>
<td>4</td>
<td>4</td>
<td>10</td>
<td>34.7±7</td>
<td>24.5±5</td>
<td>34.6±9</td>
</tr>
<tr>
<td>Subsoil</td>
<td>2</td>
<td>42</td>
<td>17</td>
<td>13</td>
<td>2</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>17</td>
<td>33.6±6</td>
<td>17.7±7</td>
<td>49.9±9</td>
</tr>
</tbody>
</table>

* CV - Coefficient of Variation

* Units of K are [µg<sub>1-L</sub>/kg], and units of n are [-]

3.2. Reference Isotherm and Scale Factors

A summary of sorption isotherm parameters and scale factors from direct and indirect scaling procedures and their statistics are presented in Table 3. Because the mean of scale factors is always 1 (compare to eq. 4), the range of scale factors with the coefficient of variation is given. CVs of scale factors α appear to be lower than CVs of K in Table 2, and higher than CVs of n in consideration of residual sum of squares. As shown in Table 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 that for sandy soils, successful scaling of sorption isotherms is possible.

Table 3. α and reference isotherms from direct and indirect scaling procedures, and statistical parameters.

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Horizon</th>
<th>Sample size</th>
<th>Direct scaling procedure</th>
<th>Indirect scaling procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>α Range [-] CV [%]</td>
<td>SE Range [-] CV [%]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-SI&lt;sup&gt;+&lt;/sup&gt;</td>
<td>α&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Adj. R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>SI&lt;sub&gt;mixed&lt;/sub&gt;&lt;sup&gt;#&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cd</td>
<td>topsoil</td>
<td>50</td>
<td>0.67 ± 13</td>
<td>85 ± 10</td>
</tr>
<tr>
<td></td>
<td>subsoil</td>
<td>50</td>
<td>0.87 ± 16</td>
<td>92 ± 13</td>
</tr>
<tr>
<td>Zn</td>
<td>topsoil</td>
<td>50</td>
<td>0.71 ± 14</td>
<td>88 ± 11</td>
</tr>
<tr>
<td></td>
<td>subsoil</td>
<td>50</td>
<td>0.81 ± 14</td>
<td>75 ± 11</td>
</tr>
<tr>
<td>Cu</td>
<td>topsoil</td>
<td>50</td>
<td>0.23 ± 5</td>
<td>78 ± 13</td>
</tr>
<tr>
<td></td>
<td>subsoil</td>
<td>50</td>
<td>0.39 ± 10</td>
<td>89 ± 32</td>
</tr>
</tbody>
</table>

* Reference sorption isotherm, ^ Scaling efficiency, # Sorption isotherm derived from mixed sample
The values of "Adj. $R^2$" for indirect scale factors are low, indicating only weak correlation between measured soil properties and scale factors. The reasons could be a relatively small sample size and low CVs of soil properties, among other things. The reference sorption isotherms of the direct scaling procedure correspond quite well with sorption isotherms of the indirect scaling procedure (measured at mixed soil samples). This demonstrates that scale means are meaningful estimators to upscale soil sorption properties from point measurements to the field scale.

3.3. Evaluation of Heavy Metal Transport

The simulated heavy metal concentrations are shown in Figure 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 extent of transport variability is in the order of Scenario I > II > III. These results indicate that the application of scale factors for sorption isotherms, especially indirect scale factors, causes a certain reduction of the variability of heavy metal retardation in soil, while the typical transport behavior of the metals is maintained.

Unlike Cd and Cu, Zn shows a very good match between model results simulated with the original topsoil sorption data or scale factors, regardless of the scaling procedure. This is very probably due to two reasons. First, Zn topsoil has a scaling efficiency of 88% (Table 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 $CV$s of $\alpha$ and $\alpha_n$ (Table 3). Also, Nanos and Martin (2012) found that Zn concentrations in soil are not as spatially variable as Cd and Cu concentrations.

On the other hand, the simulation scenarios for the highly spatially variable heavy metal Cu demonstrate a disadvantage of sorption scale factors. Maximum Cu concentration has already been transported to a depth larger than 60 cm only in column 13 (from the left of the transect, Fig. 1) if simulated with the original sorption data (Scenario I). If simulated with direct scale factors (Scenario II) or indirect scale factors (Scenario III), respectively, Cu in column 13 traveled only slightly deeper or to a rather similar depth, compared to surrounding columns (Fig. 1). The reason for this behavior may be explained by comparing Freundlich parameters $K$ and scale factors. The original Freundlich $K$ at column 13 is 98.7 µg L$^{-n}$/kg. Obviously, Cu retardation at this point (column 13) is relatively low. In contrast, the mean $K$ of a directly calculated reference isotherm and $K$ of a mixed sample are 244.8 and 274.8 µg L$^{-n}$/kg, respectively. I.e., the ratios are 0.4 and 0.36, respectively. But the corresponding squared scale factors $\alpha^2$ (eq. 2) are 0.82 and 0.91. Thus, using scale factors, a much stronger retardation of Cu is simulated in column 13. This shows that scale factors, and especially scale factors of the applied indirect scaling procedure (uncertain as indicated by low Adj. $R^2$, Table 3), are not well suited to describe extreme situations at single points in space.

Summarized, the simulated scenarios show that scale factors are well suited for predicting spatially variable retardation and transport of heavy metals in soil, although a certain reduction of variability is to be expected. In the case of extreme situations, transport simulations with scale factors are not well suited to describe the depth distribution of heavy metal concentrations.
Figure 1. The simulation scenarios of heavy metal transport with I: the original sorption procedure, II: the direct scaling procedure, and III: the indirect scaling procedure.
4. Conclusions

We demonstrated that the calculation of scale factors is a convenient and effective method (due to high scaling efficiency) for deriving the mean sorption isotherm at the 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, for example, in the case of Zn. In extreme situations (very weak heavy metal sorption) at single points, scale factors may not be sufficiently effective to simulate sorption or retardation. In such a case, the indirect scaling procedure especially fails because of the high uncertainty of the multiple regression. However, in general, the applied indirect scaling procedure tends to even 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 such as a specific soil surface area.

References


