



# Uncertainties associated with lacking data for predictions of solid-solution partitioning of metals in soil



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## HIGHLIGHTS

- Estimates of metal solid-solution partitioning sensitive to soil property data.
- Uncertainty mainly due to lacking reactive metal contents, pH, and organic matter.
- Soil solution concentrations of oxy-anions highly influenced by oxide contents.
- Clay contents had least effects on solid-solution partitioning of metals in soil.

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## ABSTRACT

Soil properties, i.e., pH and contents of soil organic matter (SOM), dissolved organic carbon (DOC), clay, oxides, and reactive metals, are required inputs to both mechanistic and empirical modeling in assessing metal solid-solution partitioning. Several of these properties are rarely measured in site-specific risk assessment. We compared the uncertainties induced by lacking data on these soil properties in estimating metal soil solution concentrations. The predictions by the Orchestra framework were more sensitive to lacking soil property data than the predictions by the transfer functions. The deviations between soil solution concentrations of Cd, Ni, Zn, Ba, and Co estimated with measured SOM and those estimated with generic SOM by the Orchestra framework were about 10 times larger than the deviations in the predictions by the transfer functions. High uncertainties were induced by lacking data in assessing solid-solution partitioning of oxy-anions like As, Mo, Sb, Se, and V. Deviations associated with lacking data in predicting soil solution concentrations of these metals by the Orchestra framework reached three-to-six orders of magnitude. The solid-solution partitioning of metal cations was strongly influenced by pH and contents of organic matter, oxides, and reactive metals. Deviations of more than two orders of magnitude were frequently observed between the estimates of soil solution concentrations with the generic values of these properties and the estimates based on the measured data. Reliable information on these properties is preferred to be included in the assessment by either the Orchestra framework or transfer functions.

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## 1. Introduction

Consumption of vegetables is one of the most important sources for metal accumulation in humans (Cohen et al., 1998; Swartjes et al., 2007). The exposure via vegetable consumption is therefore included in a number of models such as CSOIL in the Netherlands, CLEA in the UK, and RBCA Tool Kit in the US (Carlson and Swartjes, 2007; Brand et al., 2007; DEFRA and EA, CLR 10, 2002; US EPA, 1996). In such models, metal concentrations in vegetables are empirically estimated without evaluation of metal absorption by plant roots while root uptake is the main mechanism for metal accumulation in plants (Smolders, 2001;

Malecka et al., 2008; Swartjes et al., 2007). Assessment of root uptake is needed to obtain a mechanistic understanding of metal accumulation in vegetables, requiring reliable estimates of the amount of metals available for uptake. The bioavailability of metals in soil is determined by the solid-solution partitioning (Gerritse and Vandriel, 1984; Sauvé et al., 2000a; Adamo et al., 2002; Bonten et al., 2008; Gaw, 2009; Kabata-Pendias and Pendias, 2001; Adriano, 2001). Therefore, it is important to predict metal solid-solution partitioning in site-specific risk assessment as a first step toward mechanistic modeling of plant uptake and ultimately human exposure.

Metal solid-solution partitioning can be predicted by either empirical or mechanistic modeling approaches using transfer functions or multi-surface complexation models, respectively. Transfer functions empirically relate soil solution concentrations to the corresponding reactive concentrations in soil and soil properties (Sauvé et al., 2000a, 2000b; Boekhold et al., 1993; Groenenberg et al., 2010). Mechanistic

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multi-surface modeling frameworks consist of different complexation models that simulate metal sorption to various reactive surfaces, i.e., organic matter, metal(hydr)oxides, or clay (Dijkstra et al., 2009).

Both multi-surface complexation models and transfer functions require input data on soil properties, including pH and contents of soil organic matter (SOM), dissolved organic carbon (DOC), clay, oxides, and reactive metals. However, in common practice of contaminated site investigations, pH and the content of clay and SOM are not always measured, while the concentration of oxides, DOC, and reactive metals is hardly determined (Swartjes et al., 2012; Spijker, 2012). The limited data availability restricts the application of these modeling approaches to site-specific assessment.

The present study therefore aimed to evaluate uncertainties induced by lacking data on soil properties in assessment of metal solid-solution partitioning, which determines metal concentrations relevant for plant uptake. The uncertainties were assessed for the predictions by both empirical transfer functions and mechanistic multi-surface complexation models. Deviations were examined between the estimates of metal soil solution concentrations based on measurements and the estimates obtained by using generic values for contents of SOM, clay, and oxides, pH, and predicted concentrations of DOC and reactive metals.

## 2. Materials and methods

### 2.1. Transfer functions and multi-surface complexation models

#### 2.1.1. Empirical transfer functions

Empirical transfer functions of solid-solution partitioning have usually been derived according to the Freundlich model (Groenenberg et al., 2010). The transfer functions developed for the Netherlands by Groenenberg et al. (2012) were used in the present study because they were established based on an extensive experimental data set covering a wide range of soil types and environmental conditions. These transfer functions were derived according to the general following equation, taking into account a large set of potential variables:

$$\log C = \alpha_0 + \alpha_1 \cdot \log Q + \alpha_2 \cdot \log \text{SOM} + \alpha_3 \cdot \log \text{clay} + \alpha_4 \cdot \log \text{AlFe}_{\text{ox}} + \alpha_5 \cdot \log \text{DOC} + \alpha_6 \cdot \text{pH} \quad (1)$$

with C (mol L<sup>-1</sup>): soil solution concentration; Q (mol kg<sup>-1</sup>): reactive metal concentration, extracted with 0.43 M HNO<sub>3</sub>; SOM (%): soil organic matter content; DOC (mg L<sup>-1</sup>): dissolved organic carbon content; clay (%): clay content; and AlFe<sub>ox</sub> (mmol kg<sup>-1</sup>): sum of oxalate extractable Al and Fe oxides. Coefficients  $\alpha_0$ ,  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ,  $\alpha_4$ ,  $\alpha_5$ , and  $\alpha_6$  determined by Groenenberg et al. (2012) were used for empirical assessment of metal solid-solution partitioning (Table S1).

#### 2.1.2. Multi-surface complexation models

In the present study, we used the multi-surface model setup of Dijkstra et al. (2009) implemented in the model framework Orchestra (Objects Representing Chemical Speciation and TRANsport) (Meeussen, 2003). This multi-surface complexation framework takes into account aqueous speciation, mineral equilibria, and sorption of ions to particulate and dissolved organic matter, clay, and Al/Fe-(hydr)oxides. The model setup and parameterization as well as the derivation of model input are briefly given in Table S2 and described in more detail in Dijkstra et al. (2009) and Groenenberg et al. (2012).

### 2.2. Data set

The data set used in the present study covers measurements on total metal concentrations in aqua regia, reactive metal concentrations (extracted with 0.43 M HNO<sub>3</sub>), and soil solution concentrations. These data were available for a number of metals, namely Cd, Cu, Ni, Pb, Zn, As, Ba, Co, Cr, Mo, Sb, Se, and V. The data set also provided

measurements on soil properties, i.e., pH and contents of SOM, DOC, clay, and Fe/Al/Mn-oxide. The samples were collected in the field and represent various conditions of sandy and agricultural soil in the Netherlands (Table 1).

### 2.3. Scenario analyses

The full set of measured soil properties was used to predict soil solution concentrations only in one scenario, namely benchmark scenario (S\*). Seventeen other scenarios were defined with predicted or generic values for DOC, SOM, clay, oxides, and/or pH (scenarios S1–S16), and reactive metal concentrations (scenario S17). A summary of the characteristics of all the scenarios is presented in Table 2.

In SOM (S1–S5), clay (S6–S9), and oxide (S10–S12) scenarios, maximum, minimum, and average values from the above-mentioned data set have been selected, representing 'low', 'high', and 'average' levels. Therefore, these generic values could be considered to be representative of soil quality at the site investigated. Default values for SOM (10%) and clay (25%) contents as assumed for the Dutch standard soil were included in one of the scenarios regarding SOM and clay (Spijker, 2012). In SOM scenarios (S1–S5), DOC contents were predicted based on the following empirical relation derived by Römken et al. (2004):

$$\log \text{DOC} = 2.04 + 0.73 \cdot \log \text{SOM} - 0.17 \cdot \text{pH} \quad (2)$$

where DOC (mg CL<sup>-1</sup>): dissolved organic carbon content and SOM (%): soil organic matter content.

In the pH scenarios, measured pH values were replaced by default values assigned for sand (5.5), clay (6.5), and peat (6) (Römken et al., 2007). Moreover, a default scenario with generic values for all these soil properties was defined (scenario S16). In this scenario, the contents of SOM and clay assigned to the Dutch standard soil, i.e., 10% and 25%, respectively, were used (Spijker, 2012); the oxide content was set to the average value, while the DOC content was calculated using Eq. (2); and a pH value of 6 as suggested by Römken et al. (2007) was applied to this scenario. In scenarios S1–S16, reactive metal concentrations in 0.43 M HNO<sub>3</sub> extraction were used as inputs to both the transfer functions and the Orchestra framework.

Uncertainties in the estimations of soil solution concentrations by using total metal concentrations in aqua regia extraction were assessed in scenario S17 (aqua regia scenario). In this scenario, reactive metal concentrations were predicted from total metal concentrations in soils and total-reactive converting factors. The converting factors were derived from regression between the reactive metal concentrations and the total metal concentrations in the data set. The estimates of reactive metal concentrations were then used as inputs to the transfer functions and the Orchestra framework.

### 2.4. Uncertainty analyses

Uncertainties induced by lacking data were assessed by investigating the deviations in the estimates of metal soil solution concentrations with varying input values. The deviations were evaluated by calculating the root mean square residual (RMSR) reflecting the differences between soil solution concentrations predicted in scenarios S1–S17 and those obtained in the benchmark scenario S\*. High RMSR values indicate a large deviation of the estimates in the scenarios S1–S17 from those in the benchmark scenario S\*.

## 3. Results

The residuals representing the deviations between the estimate of metal soil solution concentrations in the benchmark scenario S\* and the estimate in DOC (S1), average SOM (S4), average clay (S8), average oxide (S12), peat pH (S15), default (S16), and aqua regia (S17) scenarios are given in Table 3. The results for all scenarios are

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