Multi-surface modeling of Ni(II) and Cd(II) partitioning in soils: Effects of salts and solid/liquid ratios

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HIGHLIGHTS

- A multi-surface model predicts Ni/Cd desorption in soils with wide S/L ratios.
- The model's performance has an order of 0.01 M $CaCl_2$ > 0.01 M $NaNO_3$ > water.
- Adding soil background cations significantly promote the model's prediction.
- The model has potential applications to solid/liquid ratio at field conditions.

GRAPHICAL ABSTRACT
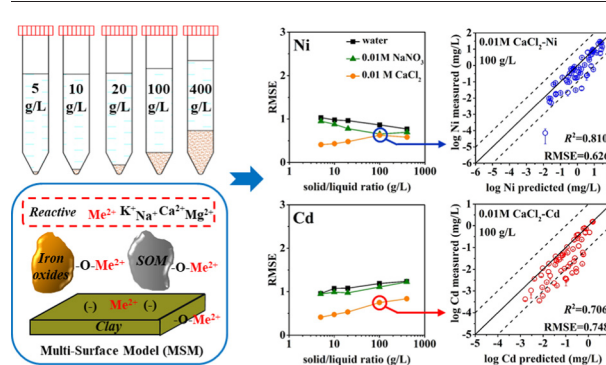
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ABSTRACT

Metal partitioning in soils is a key process controlling metal bioavailability and mobility and is greatly influenced by the solid/liquid ratio. However, metal partitioning is difficult to describe either by a simple partition coefficient or by isotherm adsorption equations. This study investigated the solubility of Ni(II) and Cd(II) in 19 soils as a function of three extraction reagents (water, 0.01 M $NaNO_3$, and 0.01 M $CaCl_2$), five solid/liquid ratios (5–400 g/L) and field condition extracted by Rhizon samplers. Thermodynamically based multi-surface models (MSMs) that included generic parameters were used to describe metal partitioning under the studied conditions. The results showed that Ni/Cd solubility depended on the soil type, extraction reagent, and solid/liquid ratio. Soil major background cations (especially Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}) had a significant effect on the model's prediction ability. The MSM was able to predict the extractable metal in 0.01 M $CaCl_2$ in various soils at different solid/liquid ratios when soil background cations were included in the calculation; without the background cations, the model was able to predict metal partitioning only at solid/liquid ratios of <100 g/L. In addition, the model failed to predict water-extracted and 0.01 M-$NaNO_3$-extracted Ni/Cd if background cations were not included, but could reasonably do so if they were included. More importantly, after the background cations were included, MSMs relatively well predicted the Ni/Cd content in soil pore water under 80% field capacity conditions with water as the solution matrix.

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1. Introduction

The bioavailability and mobility of heavy metals in soils and sediments are largely determined by the solid/liquid partitioning of the

metals (Duffner et al., 2014) and by soil properties, especially pH and soil composition (Dijkstra et al., 2009; Rodrigues et al., 2010; Sauvé et al., 2000). Studies of the solid/liquid partitioning of metals mostly rely on batch adsorption experiments at defined solid/liquid ratios, using intensive mixing followed by separation of the aqueous and solid phases (Allen et al., 1995; Papini et al., 1999). However, numerous studies have demonstrated that the solid/liquid ratio plays a key role in metal partitioning in soils and sediments, with a higher dilution in most cases resulting in an increase in the amount of extractable metal (Bordas and Bourg, 2001; Cheng et al., 2006; Jalali and Matin, 2015; Mizutani et al., 2017). However, metal desorption is often non-linearly related to the solid/liquid ratio (Bordas and Bourg, 2001; Chang et al., 2002; Fest et al., 2008; Fotovat et al., 1997), which in turn has an effect on the concentrations of abundant soil cations (such as Ca^{2+} and Mg^{2+}) and of dissolved organic carbon (DOC), both of which may compete or complex with heavy metal ions (Ettler et al., 2007; Fest et al., 2008; Fotovat et al., 1997; Gommy et al., 1998; Kaiser et al., 2001; Mizutani et al., 2017). As a result, it is difficult to predict metal dissolution for a wide range of solid/liquid ratios using a distribution coefficient (K_d) or traditional adsorption isotherm equations, such as the Langmuir or Freundlich equations (Chang et al., 2002; Fotovat et al., 1997; Yin, 2002; You et al., 1999).

In the last two decades, considerable progress has been made in the development and parameterization of surface complexation models of ion binding onto the reactive surfaces in soils, including soil organic matter (SOM) (Ge et al., 2005; Gustafsson, 2001; Kinniburgh et al., 1999; Koopal et al., 2005; Tipping, 1994; Van Riemsdijk et al., 2006), oxide minerals (Dzombak and Morel, 1990; Hiemstra and van Riemsdijk, 1999; Hiemstra and VanRiemsdijk, 1996; Nano and Strathmann, 2006; Tonkin et al., 2004), and clay minerals (Gu and Evans, 2007; Spathariotis and Kallianou, 2001). Multi-surface models (MSMs) combine these ion-binding models of the various soil components to predict the partitioning and speciation of metals in natural environments (Di Bonito et al., 2018; Groenenberg and Lofts, 2014; Weng et al., 2001). Because the binding constants are thermodynamically based, MSMs are independent of environmental conditions (e.g. pH and ionic strength) and suitable for predictions outside the range of conditions used to fit the parameters (Koopal and Avena, 2001). In the study of Groenenberg et al. (2012), MSMs were able to predict the dissolved concentrations of 13 trace elements (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V, Zn) in a wide range of European soils. Duffner et al. (2014) showed that the predicted free Zn^{2+} concentration in solution agreed well with the results measured using a soil column Donnan membrane technique, even for low zinc-containing soils (0.1–21 mg Zn/kg soil). In other studies, the model-predicted dissolved Cd, Cu, Pb, and Zn concentrations in various soils were consistent with those of the labile metal pool, measured using the stable isotope dilution technique (Ren et al., 2017; Ren et al., 2015).

One of the most important input parameters of MSMs is the binding-site concentration of each soil component (e.g. SOM, clays, and oxide minerals), which need to be transformed from surface-based parameters (site/nm^2) to solution concentrations (mol/L) based on the suspension density (or solid/liquid ratio). Most previous MSM studies employed a constant solid/liquid ratio, for example, 4 g/L (Gu et al., 2014), 66.7 g/L (Khai et al., 2008), and 100 g/L (Cui and Weng, 2015; Groenenberg et al., 2012; Groenenberg et al., 2017) in batch adsorption experiments, or 100 g/L (Ren et al., 2015) and 500 g/L (Duffner et al., 2014; Fest et al., 2008; Weng et al., 2001) in soil column Donnan membrane experiments. Although the model performed well in those studies, the effect of the solid/liquid ratio on the prediction has not been systematically investigated. More importantly, whether MSMs can predict metal desorption under field conditions is still unclear.

In this study, the effects of solid/liquid ratios on the desorption of Ni (II) and Cd(II) were investigated in 19 Chinese soils with a wide range of soil properties. The efficacies of different extractants (water, 0.01 M $NaNO_3$ and 0.01 M $CaCl_2$) were also compared. MSMs were employed

to predict metal desorption under various conditions. The specific objectives of this study were: 1) to examine the ability of MSMs to predict Ni(II) and Cd(II) desorption from soils as a function of different solid/liquid ratios, extractants, and metal concentrations, and 2) to better understand the factors that control the partitioning of metals in solid and solution phases.

2. Materials and methods

2.1. Soil characteristics

The physicochemical properties of the 19 Chinese topsoil samples (0–20 cm depth) investigated in this study are listed in Table 1 and included pH, SOM, cation exchange capacity (CEC), dithionite-citrate-bicarbonate extractable Fe content (DCB-Fe), oxalate-extractable Fe content (ox-Fe), and the clay fraction content (Bonten et al., 2008). DCB-Fe and ox-Fe represent total and amorphous iron oxides, respectively. The amount of crystalline iron oxides was estimated by subtracting ox-Fe from DCB-Fe. The reactive major cation pool (K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+}) was determined using 0.43 M HNO_3 (soil:liquid ratio = 1:10, 2 h of shaking) (Duffner et al., 2014).

All 19 soil samples were spiked with $Ni(NO_3)_2$ to obtain pollution levels of 20, 200, and 500 mg Ni/kg soil; 12 soil samples were spiked with $Cd(NO_3)_2$ to achieve pollution levels of 0.5, 1, 5, 10, and 20 mg Cd/kg soil. The Ni(II)- and Cd(II)-contaminated soils represented soils with high and low heavy metal contents, respectively. After aging for 30 days with a water capacity of ~80%, the soils were air dried and a portion then sieved over a 2-mm sieve for further extraction experiments. The total reactive Ni(II) and Cd(II) pools were determined following metal extraction with 0.43 M HNO_3, prepared as described above (Duffner et al., 2014).

2.2. Soil extraction experiments

Unbuffered salt solutions are widely used to extract heavy metals from soils. In this study 0.01 M $NaNO_3$ and 0.01 M $CaCl_2$ were used as the extraction solutions and deionized water for comparison. The metal extractions were conducted in batch experiments with solid/liquid ratios of 5, 10, 20, 100, and 400 g/L. The soil samples and extraction solutions were added to polyethylene centrifuge tubes in predetermined weights and volumes, respectively. The suspensions were shaken for 2 h at 20 °C and then separated by centrifugation and filtration (0.22-μm nylon filters). The solution pH was recorded immediately (Orion 3-star, Thermo Scientific, USA). The dissolved Ni(II) concentration was measured by flame Atomic Absorption Spectrometry (AAS; Solaar M6, Thermo Fisher Scientific, MA, USA), and the dissolved Cd(II) concentration by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (NEXION 300, Perkin Elmer, USA). The amount of dissolved organic carbon (DOC) extracted by water, 0.01 M $NaNO_3$ and 0.01 M $CaCl_2$ was measured using a total organic carbon analyzer (Element vario TOC cube). All experiments were conducted in triplicate.

2.3. Soil pore water collection

To examine the applicability of the MSMs to metal-partitioning moisture conditions such as exist in the field, soil pore water was collected using Rhizon soil moisture samplers and standard syringes (Rhizosphere Research Products, The Netherlands) after equilibration of the soils for 30 days at ~80% field capacity. Fifteen ml of soil pore water was extracted. The Ni(II) or Cd(II) concentrations of the soil solutions were determined by AAS and ICP-MS, respectively. The amount of DOC in pore water was also recorded.