



Kinetics of heavy metal adsorption and desorption in soil: Developing a unified model based on chemical speciation

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Abstract

Predicting the kinetics of heavy metal adsorption and desorption in soil requires consideration of multiple heterogeneous soil binding sites and variations of reaction chemistry conditions. Although chemical speciation models have been developed for predicting the equilibrium of metal adsorption on soil organic matter (SOM) and important mineral phases (e.g. Fe and Al (hydr)oxides), there is still a lack of modeling tools for predicting the kinetics of metal adsorption and desorption reactions in soil. In this study, we developed a unified model for the kinetics of heavy metal adsorption and desorption in soil based on the equilibrium models WHAM 7 and CD-MUSIC, which specifically consider metal kinetic reactions with multiple binding sites of SOM and soil minerals simultaneously. For each specific binding site, metal adsorption and desorption rate coefficients were constrained by the local equilibrium partition coefficients predicted by WHAM 7 or CD-MUSIC, and, for each metal, the desorption rate coefficients of various binding sites were constrained by their metal binding constants with those sites. The model had only one fitting parameter for each soil binding phase, and all other parameters were derived from WHAM 7 and CD-MUSIC. A stirred-flow method was used to study the kinetics of Cd, Cu, Ni, Pb, and Zn adsorption and desorption in multiple soils under various pH and metal concentrations, and the model successfully reproduced most of the kinetic data. We quantitatively elucidated the significance of different soil components and important soil binding sites during the adsorption and desorption kinetic processes. Our model has provided a theoretical framework to predict metal adsorption and desorption kinetics, which can be further used to predict the dynamic behavior of heavy metals in soil under various natural conditions by coupling other important soil processes.

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1. INTRODUCTION

In soil environment, the dynamic behavior of heavy metals is usually affected by multiple coupled physical and chemical processes, such as flow transport, diffusion

processes, uptake by plant roots, and chemical reactions such as adsorption/desorption and precipitation/dissolution. Those reactions/processes may affect metal kinetic behavior at different time scales and are highly dependent on specific field conditions. In general, transport-controlled kinetics is important in field conditions for controlling the dynamic behavior of heavy metals, which should be carefully considering when modeling the kinetic

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behavior of heavy metals in soil (Selim and Amacher, 1988; Sparks, 1989; Buffle et al., 2009; Selim, 2014). Typical mechanisms contributing to the transport kinetics may include mass flow, molecular diffusion, dispersion, etc. (Selim, 2014), which may affect the dynamic behavior of heavy metals at different time and spatial scales. In solution phase, heavy metals may first diffuse through the diffusion layer, then undertake a series of reactions in the reaction layer, and finally sorb onto the solid surfaces, indicating complex dynamic processes involving physical, chemical and even biological processes/reactions (Buffle et al., 2009). To accurately predict the kinetic behavior of heavy metals in soil, an adequate kinetics model should consider the coupled chemical, physical and biological processes occurring in soil environments.

Among typical chemical reactions in soil, the adsorption/desorption reaction is a key process controlling the reactivity and bioavailability of heavy metals in soil. Extensive work has been done to predict the equilibrium of heavy metal adsorption in soils, including statistical regression models (Janssen et al., 1997; McBride et al., 1997; Sauve et al., 2000, 2003) and mechanistically based chemical models considering metal surface complexation reactions with the major soil adsorbents such as soil organic matter (SOM), Fe and Al (hydr)oxides (Weng et al., 2001; Gustafsson et al., 2003, 2014; Tipping et al., 2003; Shi et al., 2007; Alessi and Fein, 2010; Duffner et al., 2014; Groenenberg and Lofts, 2014). However, due to the frequently varying reaction conditions in soil environments, the equilibrium assumption may not be appropriate for metal adsorption and desorption reactions in soil (Sparks, 1989), and modeling approach based on instantaneous equilibrium was not able to describe the time-dependent metal adsorption/desorption reactions in soil (Shi et al., 2005). The rates of metal release from soil to solution, controlled by the combination of both (re)adsorption and desorption reactions, may affect the bioavailability of metal ions in soil (Zhang et al., 1998). In the natural environment, the slow release of metal ions from the organic matter may limit the rates of uptake by biota (Anderson and Morel, 1982; Iwai et al., 2015). Therefore, for a better risk assessment and design of remediation techniques for contaminated sites, a quantitative understanding of the kinetics of heavy metal adsorption and desorption reactions in soil under varying environmental conditions is required, which provides basis for further predicting the dynamic behavior of heavy metals in coupled chemical and physical processes in soil.

Soil organic matter (SOM) is probably the most important soil component controlling metal adsorption and desorption in soil, and its dominant role on controlling metal partitioning has been extensively studied with both chemical equilibrium models (Weng et al., 2001, 2004; Gustafsson et al., 2003; Tipping et al., 2003; Shi et al., 2007, 2013a; Cabaniss, 2009, 2011; Xiong et al., 2013) and advanced spectroscopic techniques (Xia et al., 1997; Fulda et al., 2013; Xiong et al., 2013; Gustafsson et al., 2014; Fan et al., 2016). Among all SOM binding sites, the carboxylic and phenolic sites are two of the most important functional groups controlling metal binding, and each type

of sites or binding sites formed through various combinations of those two types of sites have distinct thermodynamic properties, such as proton and metal binding constants (Tipping, 1994; Benedetti et al., 1995; Kinniburgh et al., 1999; Gustafsson, 2001; Milne et al., 2001; Koopal et al., 2005; Carbonaro and Di Toro, 2007; Atalay et al., 2009, 2013; Carbonaro et al., 2011; Tipping et al., 2011). To reflect the heterogeneity of both carboxylic and phenolic sites, chemical equilibrium models assume either a discrete or a continuous distribution of the binding sites for each group of sites (Tipping, 1994; Benedetti et al., 1995; Gustafsson, 2001). Previous equilibrium studies on predicting metal adsorption on SOM employing NICA-Donnan (Benedetti et al., 1995), Windermere Humic Aqueous Model (WHAM) (Tipping, 1994), and the Stockholm Humic Model (Gustafsson, 2001) were mainly based on the comparison of macroscopic experimental parameters, with little insight on metal distribution among various SOM binding sites (Tipping and Hurley, 1992; Gustafsson, 2001; Xiong et al., 2013). Metal binding to various SOM sites may have different metal adsorption and desorption rates and may significantly affect the kinetic behavior of metal ions in dynamic soil environments (Shi et al., 2008, 2013b). So far, how those individual SOM binding site control both adsorption and desorption rates of various heavy metals under various reaction chemistry conditions is still largely unknown, which limits our ability to accurately predict the dynamic behavior of heavy metals in soil.

Soil minerals, such as Fe and Al (hydr)oxides, are other important soil components affecting metal adsorption and desorption reactions (Groenenberg and Lofts, 2014). Among typical soil Fe minerals, ferrihydrite has a relatively high surface area compared to goethite and thus a relatively higher number of binding sites for metal complexation (Cornell and Schwertmann, 2004). In soil the Al (hydr)oxides generally have comparable amount as the Fe (hydr)oxides and thus may have comparable importance for metal binding as the Fe (hydr)oxides (Groenenberg and Lofts, 2014). A number of surface complexation models (SCMs) have been developed to describe metal ion reactions with metal (hydr)oxides (Westall and Hohl, 1980; Dzombak and Morel, 1990; Goldberg, 1992; Hiemstra and van Riemsdijk, 1996; Venema et al., 1996; Lofts and Tipping, 1998; Wang and Giammar, 2013), which differ in their formulations of the charge distribution, surface potential, and adsorption sites/locations. The diffuse layer model (DLM) and the constant capacitance model (CCM) are among the SCMs developed to describe metal binding to mineral surfaces (Dzombak and Morel, 1990; Lofts and Tipping, 1998). The Charge Distribution Multi-Site Complexation (CD-MUSIC) model (Hiemstra and van Riemsdijk, 1996) is one of the advanced and mechanistically robust SCMs, and has been reported to provide better predictions of metal complexation with ferrihydrite than some other SCMs (Gustafsson et al., 2011). Despite the large volume of studies on the equilibrium of metal ion binding to soil minerals (e.g. (Dzombak and Morel, 1990; Hiemstra and van Riemsdijk, 1996; Dyer et al., 2003; Ponthieu et al., 2006; Hiemstra and Van Riemsdijk, 2009; Gustafsson et al., 2011; Tiberg et al., 2013; Tiberg and Gustafsson,

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