Characterization of the dissociation kinetics of Cd and Ni in soils based on diffusive gradients in thin films technique

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ABSTRACT

A new theoretical method was established for the combinatorial calculation of the dissociation rate constant (K_{-1}) of the metal-organic complexes (MLs), the concentration of free ionic soil metals (C_M), the labile concentration of soil metal-organic complexes (C_{ML}) based on diffusive gradients in thin-films (DGT) technique with a range of diffusive layer thicknesses (0.053–0.173 mm) in soils. The fitting results agreed well with the determined values. The values of K_{-1}, C_{ML} and C_M were calculated without other morphological analysis software and the fitting results agreed well with the determined values with some advantages such as the use of fewer hypothetical parameters, ease of calculation, the full embodiment of the contribution of MLs to the labile content. According to the results of model fitting, cation exchange capacity and soil organic matter were found to be the key environmental factors for K_{-1} values of Cd and Ni, respectively. The labile contents of Cd and Ni in soil were closely related with pH, soil organic matter and the total contents of heavy metals.

1. Introduction

Heavy metal pollution has pervaded many parts of China (Cheng, 2003). The harm of heavy metals in the soil may be related directly to their speciation and not strictly related to the total concentrations of metals (Allen et al., 1980). The bioavailability of metal ions in soil systems strongly depends on the metal binding form (King et al., 2001). Metal speciation measurement as a powerful basis was used to predict their bioavailability and risk assessment (Van et al., 2005). The dissociation kinetics of metal-organic complexes may limit the bioavailability of metal ions in natural environment (Chakrabarti et al., 1996; Shi et al., 2005). The understanding of the dissociation kinetics of metal-ligands complexes (MLs) is essential for the prediction of heavy metals bioavailability in the environment (Buzier et al., 2006; Degryse et al., 2006).

There are many methods for determining the labile speciation of heavy metals in soil, including chemical extraction (Rao et al., 2008), model calculation (such as Model VII used by WHAM (Stockdale et al., 2015), NICA–Donnan model used by ECOSAT (Fortin et al., 2010; Kalis et al., 2006), and SHM used by MINTEQ (Lourino-Cabana et al., 2014)),

voltammetric methods (such as differential pulse cathodic stripping voltammmetry (Xue et al., 2001), differential pulse anodic stripping voltammmetry (Dytrtová et al., 2008)) and isotope dilution (Frišták et al., 2013). In addition, there are some methods for calculating the migration kinetics of soil heavy metals, such as DGT induced fluxes in sediments (DIFS) (Łukasz et al., 2007), double-electric-point model for WHAM coupling (Shi et al., 2008), and the isothermal adsorption-desorption model (Wang et al., 2009). Model calculation methods require the more detailed input parameters (such as the composition of organic matter, the interaction between the targets and iron manganese oxides and/or clay minerals, the influence of accompanying ions on the targets), however, these parameters are difficult to obtain accurately (Tian et al., 2017). Selection of the extracting reagents of chemical extraction bears directly on the measurement of metal speciation in soil (Vodyanitskii, 2006). For the electrochemical methods and isotope dilution methods, the soil matrix generates the strong interference in the process of metal speciation measurement by in soil (Buffle and Tercier-Waeber, 2005; Huang et al., 2004).

DGT, an in-situ passive sampling technique based on Fick's first law for the calculation of the labile heavy metals in soils, is an ideal tool to

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simulate the bioavailability of heavy metals by plants (Luo et al., 2011). Compared to the traditional chemical extraction techniques, DGT incorporates both static and dynamic processes (Luo et al., 2011). The adsorption-dissociation process of MLs in soil solution can be expressed by DGT technique (Chen et al., 2014; Zhang et al., 2001). In most cases, the concentration of labile heavy metals is indicated by the balance flow of heavy metal during a certain period. Zhang et al. proposed the DGT technique with the different thicknesses of diffusion layers which based on the assumption that only the free metal ion and not the metal complex reacts with the DGT binding resin to determine the dissociation kinetics rate constant (K_{-1}) of MLs (Zhang et al., 2001). However, this method involves many calculation parameters and less experimental results in one formula. Therefore, overfitting in the calculation process is ineluctable (Scally et al., 2003). The calculation formula usually underestimates the potential supply of dissociated soil MLs. Warnken proposed another calculation method combining with WHAM for the calculation of K_{-1} (Warnken et al., 2007). The K_{-1} value of plutonium-organic matter complex Cusnir was calculated by the Warnken's method (Cusnir et al., 2016). Based on the DIFS model, the calculated values of the K_{-1} for five types of soils were obtained by Ernstberger et al. (2005).

In this study, a new calculation method for the labile content of Ni (II) and Cd(II) by DGT in contaminated soils and the dissociation rate constant K_{-1} of MLs was established due to the different lability and dissociation kinetics of MLs for Ni(II) and Cd(II) (Luo et al., 2014; Sprynskyy et al., 2011). The relationship between the dissociation rate constant K_{-1} of MLs and the labile content of Ni(II) and Cd(II) by DGT was examined in detail to gain insight into soil processes. The calculation of dissociation kinetics and labile contents of Ni(II) and Cd(II) in soils using the proposed method will be discussed in detail.

2. Model descriptions

The DGT placed in soils can adsorb the heavy metal and the dissociated MLs in the soil solution and particles through the gradient diffusion process (Zhang et al., 1998). The DGT measured mass will be the sum of contributions of free ions both from soil solution and dissociated from MLs (Eq. (1)) (Scally et al., 2003):

$$Ma = \frac{(C_M D_M + C_{M'} D_{M\,L})At}{\Delta g} \tag{1}$$

where Ma is the accumulated amount by the binding films during time t; A is the exposed surface area; C_M is the concentration of free ionic metals in the soil solution; $C_{M'}$ indicates the ion concentration measured by the DGT with respect to MLs dissociated during time t; D_M and D_{ML} are the diffusion coefficients (cm^2 s^{-1}) of the metal ion and MLs through the gel, respectively, usually D_{ML} is equal to 20% of D_M (Scally et al., 2006), and Δg is the diffusion film thickness (cm).

According to the equations derived by Scally et al. (2003), the $C_{M'}$ in Eq. (1) can be calculated using Eq. (2):

$$C_{M'} = C_{ML}\left(1 - \exp\left[-\frac{k_{-1}(\Delta g)^2}{2D_{ML}}\right]\right) \tag{2}$$

where K_{-1} is the dissociation rate constant related to the MLs, C_{ML} indicates the dissociation concentration of the MLs in the soils, D_{ML} has the same meaning as in Eq. (1), and Δg indicates the diffusion film thickness, that is, the maximum migration distance of the MLs.

If MLs can be dissociated within Δg, it can be measured by DGT. The dissociation time of MLs varies with the changes of Δg, so that the dissociation concentration $C_{M'}$ varies consequently, as described in Eq. (2). Therefore, Δg can also be interpreted as the difference in the diffusion film thickness $\Delta g_{(b-a)}$, and $C_{M'}$ can be interpreted as the difference in the dissociation concentration of MLs with different thickness of the diffusion film. To solve Eq. (2), these differences need to be defined correctly.

According to the Fick's first law of diffusion, when only metal cations exists in the soil solution, the concentration of metal ions C_{DGT} can be calculated using the Eq. (3) (Lourino-Cabana et al., 2014):

$$C_{DGT} = \frac{Ma\Delta g}{D_M At} \tag{3}$$

where C_{DGT} is a constant value due to no dissociation of MLs in the soil solution. When D_M, A, and t are constant values, Ma is therefore reversely proportional to Δg. If C_{DGT} is calculated according to the diffusion film thickness of a, Ma^b of the DGT device with a diffusion film thickness of b can be calculated using Eq. (3).

A rise in the diffusion film thickness will cause an increase in the quantity of dissociated MLs. When the lability forms of metals in soils are metal ions and ligands, the Ma^{b+} of the DGT device with a diffusion film thickness of b (b > a) is higher than the theoretical Ma^b calculated using Eq. (3), and the balance between them can be considered as the quantity of metals dissociated by the newly increased diffusion film thickness ($\Delta g_{(b-a)}$). The concentration difference can be calculated using Eq. (4):

$$C_{DGT}^{\Delta g(b-a)} = \frac{(Ma^{b+} - Ma^b)\Delta g_{(b-a)}}{D_{ML}At} \tag{4}$$

where $C_{DGT}^{\Delta g(b-a)}$ indicates the difference of concentration of dissociated MLs between the thickness b and thickness a (b > a) (the $C_{DGT}^{\Delta g(b-a)}$ value is equivalent to the $C_{M'}$ value in Eq. (2)), Ma^{b+} indicates the actual quantity of heavy metals accumulated by the DGT device with a diffusion film thickness of b, Ma^b indicates the quantity of heavy metals accumulated by the DGT device, with a diffusion film thickness of b that is calculated using Eq. (3), and the meanings of other parameters are the same as those in Eq. (3).

According to Eqs. (2) and (4), Eq. (5) can be used to calculate the concentration of dissociated MLs when the difference of diffusion film thickness is b-a.

$$\frac{(Ma^{b+} - Ma^b)\Delta g_{(b-a)}}{D_{ML}At} = CML\left(1 - \exp\left[-\frac{k_{-1}(\Delta g_{(b-a)})^2}{2DML}\right]\right) \tag{5}$$

where $\Delta g_{(b-a)}$ indicates the thickness difference b and thickness a of diffusive layers. When DGT with different thickness diffusive films is used to measure the lability concentration of metals in soils, Eq. (5) will be achieved several times, thus nonlinear fitting can be used to calculate the parameters C_{ML} and K_{-1}. According to Eqs. (1) and (2), the C_M value is calculated. Then, the total lability concentration of soil heavy metals can be calculated using the following Eq. (6):

$$C = C_{ML} + C_M \tag{6}$$

According to Eq. (5), the maximum thickness difference $\Delta g_{max(b-a)}$ that make the MLs dissociated completely can be determined using an iterative calculation after the values for C_{ML} and $K_{-1}$are obtained. According to the initially calculated base thickness of the diffusion film, the maximum effective thickness of the diffusion film Δg_{max} for complete dissociation C_{ML} can be determined.

According to Eqs. (4) and (5), the concentration difference $C_{DGT}^{\Delta g(b-a)}$ of dissociated metal complexes MLs is influenced by two parameters: C_{ML} and K_{-1}. In Fig. 1, C_{ML} is assumed to be a constant value, 40 µg/L, and D_{ML} is equal to 20% of the cadmium ion diffusion coefficient at a temperature of 25 °C (Scally et al., 2006). K_{-1} has five gradients including 1E-2 to 1E-6 (s^{-1}). With a rise in K_{-1}, the concentration difference of dissociated MLs rapidly increases. The larger is K_{-1}, the smaller is the thickness difference $\Delta g_{max(b-a)}$ for the complete dissociation of MLs. In Fig. 2, D_{ML} is assumed to be equal to 20% of the cadmium ion diffusion coefficient at a temperature of 25 °C, K_{-1} is 1E-4 (s^{-1}), and C_{ML} ranges from 10 to 80 µg/L. The changes of C_{ML} bring about an increase of $C_{DGT}^{\Delta g(b-a)}$ but no change is observed for $\Delta g_{max(b-a)}$.