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Multisurface modeling of Ni bioavailability to wheat (*Triticum aestivum L.*) in various soils☆

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ABSTRACT

Continual efforts have been made to determine a simple and universal method of estimating heavy metal phytoavailability in terrestrial systems. In the present study, a mechanism-based multi-surface model (MSM) was developed to predict the partition of Ni(II) in soil–solution phases and its bioaccumulation in wheat (*Triticum aestivum L.*) in 19 Chinese soils with a wide range of soil properties. MSM successfully predicted the Ni(II) dissolution in 0.01 M $CaCl_2$ extracting solution ($R^2 = 0.875$). The two-site model for clay fraction improved the prediction, particularly for alkaline soils, because of the additional consideration of edge sites. More crucially, the calculated dissolved Ni(II) was highly correlated with the metal accumulation in wheat ($R^2 = 0.820$ for roots and 0.817 for shoots). The correlation coefficients for the MSM and various chemical extraction methods have the following order: soil pore water > MSM ≈ diffuse gradient technique (DGT) > soil total Ni > 0.43 M HNO_3 > 0.01 M $CaCl_2$. The results suggested that the dissolved Ni(II) calculated using MSM can serve as an effective indicator of the bioavailability of Ni(II) in various soils; hence, MSM can be used as an supplement for metal risk prediction and assessment besides chemical extraction techniques.

1. Introduction

Nickel contamination has become a worldwide concern because of nickel's hazardous effects on microorganisms (2017; Macomber and Hausinger, 2011), organisms (Chen et al., 2009; Forgacs et al., 2012; Yusuf et al., 2011) and human beings (Cameron et al., 2011; Duda-Chodak and Blaszczyk, 2008; Zambelli et al., 2016). In 2003, annual global emissions of Ni were reported to have reached 150,000 and 180,000 metric tons from natural and anthropogenic sources, respectively (Kasprzak et al., 2003). Soils are major sinks for Ni released into the environment because of their strong affinity to heavy metals (Wuana and Okieimen, 2011). The total amount of heavy metals in soils has been acknowledged as not necessarily related to the metals' potential biological risks, because only a certain fraction of soil metals is available to plants and soil fauna (Degryse et al., 2009a; Kim et al., 2015; Nolan et al., 2003; Wuana and Okieimen, 2011). Availability is affected by a number of soil properties, such as pH, soil organic matter (SOM), clay content, and cation exchange capacity (CEC) (Antoniadis et al., 2017; Sauve et al., 2000).

Over the last few decades, numerous efforts have been made to develop methods of evaluating heavy metal speciation and bioavailability in soils or sediments; for example, single and sequential extractions (Kelepertzis et al., 2015; Menzies et al., 2007; Soriano-Disla et al., 2010a), the Donnan membrane technique (Temminghoff et al., 2000; Weng et al., 2001b) and the diffusive gradient technique (DGT) (Degryse et al., 2009b; Hooda et al., 1999; Tandy et al., 2011). Among them, single extraction procedures using neutral salts (0.1 M NH_4NO_3, 0.01 M $CaCl_2$), dilute acids (0.43 M HNO_3, 0.1 M HCl), or a chelating reagent (0.05 M EDTA) have been the most widely used (Kelepertzis et al., 2015; Korzeniowska and Stanislawska-Glubiak, 2017; Milicevic et al., 2017; Pinto et al., 2015; Yang et al., 2015). Recently, 0.43 M HNO_3 was adopted by the International Organization for Standardization (ISO-17586:2016) as a standard method for the extraction of geochemically reactive elements in soils (Groenenberg et al., 2017). The DGT has also been proven to have advantages for estimating bioavailable metal fractions in soils compared with conventional extraction

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because it mimics the kinetic process of plant uptake (Qasim et al., 2016; Sun et al., 2014; Wang et al., 2014).

Despite the considerable efforts made, no method has been advocated universally because heavy metal uptake is influenced by soil properties and plant physiology. Considering these processes and a quantitative understanding of their mechanisms may be critical in determining a method that can be widely applied to estimate heavy metal availability.

Regression-based "partition" equations have been introduced to explain the possible relationships between metal solid–solution partitions and the influential factors in terms of variables (Degryse et al., 2009a; Groenenberg et al., 2010; Sauve et al., 2000). Although this modeling approach has been used widely (Ding et al., 2013; Yang et al., 2016; Zhang et al., 2016), its limitations are apparent. Because of its empirical nature, regression constants may vary with soil properties and environmental conditions. In the last two decades, mechanism-based multi-surface models (MSMs) have been developed as alternatives (Bonten et al., 2008; Groenenberg and Lofts, 2014; Weng et al., 2001a). MSMs simplify the soil matrix as a set of reactive surfaces, such as clay minerals, SOM, and iron oxides. The partition of metals at each surface was described using thermodynamic-based surface complexation models; MSMs combine these submodels additively to describe ion partitioning in the entire soil matrix. The metal binding parameters of each reactive surface can either be soil-specific or generic. MSMs have been successfully used to describe the solid–solution partition of metals in soil components (Bonten et al., 2008; Groenenberg et al., 2012; Weng et al., 2001a), predict the dissolved concentrations or free activities of metal ions in soil solution (Duffner et al., 2014; Pan et al., 2016; Rennert et al., 2017), and evaluate the performance of experimental methods (Cui and Weng, 2015; Groenenberg et al., 2017; Ren et al., 2015). However, the application of MSMs to the soil–plant system (i.e., the prediction of metal bioavailability) has not yet been performed. This is probably because of the difficulties caused by plants not linearly responding to dissolved metals or even their free activities in soil pore water. Other factors such as membrane transfer mechanisms, competing cations, rhizosphere effects, and the osmotic effect may play a role in the plant uptake process (Kim et al., 2015). Among these diverse factors, the total dissolved metal concentration in soil solution is regarded as the most significant factor in controlling plant metal uptake (Kabata-Pendias, 2011), which provides rationality for extending MSMs to soil–plant systems. This application must be examined in various soils.

In the present study, the phytoaccumulation of Ni in wheat (*Triticum aestivum L.*) grown in 19 Chinese soils with a wide range of properties was assessed using MSMs with "generic" parameters. The model's performance was compared with those of other chemical extraction techniques and a multiple regression model. The major objectives of this study were to (1) examine the predictions of the MSMs for Ni(II) partition in soil–solution phases in the selected Chinese soils, and (2) evaluate the predictability of Ni bioavailability using MSMs in the soil–plant system and compare the models with chemical methods.

2. Materials and methods

2.1. Soil analysis

Nineteen surface soils covering a wide range of soil types and properties (including five calcareous soils) were collected from central and eastern China (Fig. S1 and Table 1). The soils' pH ranged from 4.34 to 7.92 (soil:water ratio = 1:2.5). The soils' CEC was between 3.60 and 37.82 cmol kg^{-1}, which was determined using the Ba^{2+}/NH_4^+ exchange method in pH 8 buffer solution (Carter, 2007). SOM, measured using the dichromate oxidation method (Lu, 1999), was in the range 2.71–120 g kg^{-1}. Dithionite citrate bicarbonate extractable Fe (DCB-Fe) and ammonium oxalate-extractable Fe (ox-Fe) were determined as the total amount of Fe hydroxides and the amorphous Fe oxides in soils (Dijkstra et al., 2009) and were in the ranges 4.60–89.9 g kg^{-1} and 0.76–6.34 g kg^{-1}, respectively. The amount of crystalline ferric oxide was estimated from the difference between DCB-Fe and ox-Fe (Dijkstra et al., 2009). The clay fractions were in the range 1.31%–22.45%, as measured using a laser particle analyzer (LS230, Beckman Coulter). Total Ni in the soils was determined using whole acid digestion (HCl, HNO_3, HF, and $HClO_4$) (Fey et al., 2011).

2.2. Pot experiments

After collection, the soils were air-dried and passed through a 2-mm sieve. Subsequently, the soils were spiked with $Ni(NO_3)_2$ to achieve various Ni levels (0, 20, 50, 200, 500, or 1000 mg Ni/kg soil) and incubated in the dark for 30 days, maintained with a field capacity of approximately 80%. Yang 13, a common variety of wheat (*Triticum aestivum L.*) grown in the middle and lower reaches of the Yangtze River, was used as the test plant. After seed germination, five seedlings with root lengths of approximately 1 cm were transplanted to culture cups with 150 g of soil. The seedlings were grown for 7 days under a photoperiod of 16 h light at 25 °C and 75% humidity and 8 h darkness at 20 °C and 85% humidity. Plants were then carefully removed intact from the pots and cleaned thoroughly with tap water and deionized water. The roots were washed with 0.01 M Na_2H_2EDTA solution for 1 min to elute the metals adsorbed on the root surfaces and then washed with deionized water to remove extra EDTA salts (Zhang et al., 2016). Under some condition with high Ni stress, the root elongation was inhibited. Regarding the Ni toxicity to wheat root elongation, readers can refer to our recent publication (Jiang et al., 2018). The root and shoot tissues were separated and dried at 60 °C to a constant weight and digested with HNO_3–H_2O_2 (USEPA, 2012). Ni concentration was determined using atomic absorption spectrometry (AAS) (Solaar M6, Thermo Fisher Scientific, MA, USA). A reference material (bush twigs and leaves, GBW 07602, China) was also processed to evaluate the recovery rate of digestion; the results (2.02 mg/kg) were within the reference range (1.7 ± 0.4 mg/kg). All experiments were performed in triplicate.

2.3. Chemical extraction methods

In this study, four chemical extraction methods (soil pore water, 0.01 M $CaCl_2$ and 0.43 M HNO_3 extraction, and the DGT) were used to predict the bioavailability of Ni to wheat.

Soil pore water was collected *in situ* using Rhizon soil moisture samplers with standard syringes (Rhizosphere Research Products, the Netherlands). The samplers were inserted at an angle of 45° into the center of each pot on the sixth day of the 7-day pot experiment. Approximately 15 mL of soil pore water was collected and used for Ni analysis without further treatment.

After plant harvest, soil samples were air-dried and sieved through a 2-mm mesh again for further chemical extraction. The soil pH of these samples was also recorded. Single extraction with 0.01 M $CaCl_2$ or 0.43 M HNO_3 solution was performed at a soil:solution ratio of 1:10 for 2 h at 20 °C by end-over-end shaking (Groenenberg et al., 2017). Subsequently, the supernatants were collected using centrifugation and filtration with a 0.22-μm membrane.

The DGT extraction was performed according to Zhang et al. (2001) using devices from DGT Research. In summary, soil samples were remoistened to approximately 100% saturation with