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Transfer functions for estimating phytoavailable Cd and Pb in metal contaminated paddy and upland soils: Implications for phytoavailability based land management

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ABSTRACT

Partitioning of Cd and Pb in soils and dependence on soil properties were examined using representative Korean paddy and upland soils affected by abandoned mining sites. Two separate transfer functions were developed using 'high' and 'low' level data sets for the estimation of phytoavailable Cd and Pb soil pools. While the solid-solution partitioning coefficients (K_d) varied significantly with soil type and the extraction solution used to estimate availability linear regression analysis showed that soil pH influenced K_d the most. Thus simple pH control was the management option most likely to practically reduce both phytoavailable Cd and Pb. Organic matter content and oxalate extractable sesquioxides only partially influenced K_d. The transfer function derived from the 'high' level data set was most appropriate for practical application as it covered a wider range of Cd and Pb soil concentrations. While the transfer functions derived in this study generally estimated phytoavailable Cd and Pb well, literature-based transfer functions tended to overestimate metal phytoavailability. Optimal results were obtained when the transfer function was derived using local soil conditions and hence derivation of a local data based transfer function is required.

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1. Introduction

A wide range of heavy metal contaminated paddy and upland soils are still used for food crop production. From a food safety perspective, it is thus important that proper management protocols are developed for heavy metal contaminated soils. These protocols should consider the phytoavailability of heavy metals in soils which often depends on both soil chemistry and the governing soil properties. In paddy and upland soils, Cd and Pb are the two main heavy metals of perceived food safety concern, both being carcinogenic elements with designated standard limits by the Codex Alimentarius Commission (Codex Stan 210-2001, 248-2005).

Soil-solution partitioning of heavy metals is an important process determining metal bioavailability (Gerritse et al., 1983), plant uptake (Kim et al., 2012), and ecotoxicity (Lofts et al., 2004). For a soil, the soil-solution partitioning coefficient (K_d) is defined as the ratio of heavy metals distributed on the solid phase to metals distributed to the solution phase (Sauvé et al., 2000a). It is well known that heavy metals distributed to the solution phase (heavy metals in the soil pore water) exist in readily bioavailable forms amenable to plant uptake (Naidu et al., 2008) and hence increases in soil pore water metal concentrations are almost always accompanied by a decrease in the soil-solution partitioning coefficient.

Two different approaches, mechanistic models (Bonten et al., 2008; Dijkstra et al., 2004) or empirically derived transfer functions (De Vries et al., 2011; Groenenberg et al., 2010; Sauvé et al., 2000a) have been used to develop models for estimating dissolved metal concentration in soil pore water. While mechanistic models are promising predictors of soil partitioning of metals, in practice Groenenberg et al. (2010) and De Vries et al. (2011) pointed out several advantages of empirical models. Compared with mechanistic models, empirically derived models (or transfer functions) require fewer input data, since there are no iterative calculations and hence empirical models require far less computing time. Empirical models are also applicable when there is limited available data, enabling empirical models to be applied to large scale applications. In addition, given that the magnitude of metal adsorption on a soil surface is generally dependent on both the metal type and prevalent soil properties, transfer function models often require actual experimental based-determinations of solid–solution

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partitioning coefficients as input. Several researchers have tried to develop generic transfer functions to encompass a large range of soil properties into a single model. Groenenberg et al. (2010) used two large Europe databases from the UK and The Netherlands as a derivation data set for transfer functions. While prior to this, Sauvé et al. (2000a) tried to develop a generic transfer function using data compiled from around 70 literature studies. The limitations of these two attempts were that the models developed were not universal and could not be generally applied to correctly assess heavy metal soil-solution partitioning in soils from different regions. De Vries et al. (2011) derived a Cd transfer function using a representative data set of Australian soils (high pH and low organic matter) and then validated the transfer function using independent validation data. They also compared their predicted model results with measured total dissolved Cd in soil using the literature-based transfer functions derived by Sauvé et al. (2000a, b), Römkens et al. (2004), and Groenenberg et al. (2010) and found that the literature-based transfer functions underestimated dissolved total Cd in soil, while the Australian soil-based transfer function estimated dissolved Cd well. This implied that regional-based transfer functions should be developed for the most accurate assessment of metal fate in soils.

In Korea, a wide range of paddy and upland soils near abandoned metal mining sites have been contaminated and required ongoing management in order to ensure safe crop production. In order to manage these sites safely, knowledge of the heavy metal phytoavailability is required and together with empirical-based solid–solution partitioning relationships (K_d) can provide advanced site management tools. Such relationships, which are based on the distribution of total heavy metals between solid and soil solution phases, rather than the free metal ion activity, can more easily be applied in dynamic models predicting metal uptake, accumulation and leaching in response to metal inputs (De Vries et al., 2011). They also have much simpler analytical solutions, which can be used in the calculation of target loads for heavy metals (Posch and De Vries, 2009).

Developing a single, generic, transfer function for each metal for mine site contaminated soils can provide advantages for several practical applications including 1) estimation of phytoavailable metal pools and identification of influential soil properties; 2) evaluation of remediation results; and 3) development of soil amendments to reduce metal uptake by plants. For such pragmatic operational purposes, simple linear transfer functions derived using total metal concentrations in soil and phytoavailable metal concentrations determined by neutral salt extraction (i.e. 0.01 M $Ca(NO_3)_2$ extraction) would be a simpler approach and would be easier to apply than transfer functions derived using reactive metal concentrations in soil based on 0.43 M HNO_3 extractions (Tipping et al., 2003), or free metal ion activities either determined or estimated using another speciation model such as WHAM VI (Groenenberg et al., 2010; Tipping, 1994, 1998). Moreover, since mining site affected soils may contain elevated concentrations of a number of heavy metals, transfer functions need to be derived using contaminated soil data sets because the fate of heavy metals in contaminated soils may differ significantly from that in uncontaminated soils. For example, when using transfer functions derived from soils having background Cd levels, De Vries et al. (2011) found that dissolved Cd was underestimated for soils high in Cd and overestimated for soils low in Cd. Sauvé et al. (2000a) had previously reported that partitioning coefficients or models derived from low concentration data sets should not be applied for the assessment of contaminated soils and vice-versa.

Taking into account these aspects, in this study, two transfer functions for each individual metal (Cd and Pb) were derived using separate data sets from soils high in Cd and Pb, 'high level data set (HLDS)' and low in Cd and Pb, 'low level data set (LLDS)', respectively. The two transfer functions were then evaluated for the estimation of dissolved Cd and Pb in soil together with the dependence of the partitioning on soil properties including soil pH, total metal burden, organic matter (OM), dissolved organic carbon (DOC), clay content, and sesquioxides. Furthermore, the transfer functions derived in this study were compared with transfer functions derived from large literature datasets for both Cd and Pb.

2. Materials and methods

2.1. Soil samples for derivation data set

Soil samples ($n = 149$) were collected from a range of paddy ($n = 120$) and upland ($n = 29$) locations near abandoned metal mining sites from across Korea between 2006 and 2010. Surface soils (0–20 cm) were collected using a 7 cm diameter augur. Three augur samples, 10 m apart, were composited to form a single representative sample. The collected soil samples were air dried, sieved <2 mm and then stored in plastic bottles prior to analysis.

2.2. Soil samples for validation data set

In addition to the primary derivation data set described above, an additional set of soil samples ($n = 41$) were also collected from heavy metal contaminated paddy soils affected by mining sites between 2012 and 2014. These samples were collected from different geographical regions than the 'derivation data set' and were used to form a 'validation data set'. Soil sampling and pretreatment of validation soils were identical to derivation soils.

2.3. Chemical analysis

Soil pH was determined on a 1:5 soil:water (*w*/*v*) suspension using a pH meter (MP220, Mettler Toledo, Switzerland) following 1 h equilibration. Soil organic matter content was determined using the loss on ignition (LOI) method (NAAS, 2010) and soil texture was determined using a micro-pipette method (Miller and Miller, 1987). While the LOI method can potentially overestimate SOM in carbonate rich soils, the method was considered acceptable here because Korean soils are typically low in carbonate. For determination of DOC, an aliquot of the solution extracted by 0.01 M $Ca(NO_3)_2$ for phytoavailable concentration of metals were analyzed on a total organic carbon analyzer (2100S, Analytik Jena, Germany). Al/Fe/Mn oxides were determined using ICP-OES (8300DV, Perkin-Elmer, USA) after extracting the soil with ammonium oxalate (Anderson and Christensen, 1988; Janssen et al., 1997; Rayment and Higginson, 1992) followed by filtering through Whatman No. 42 (pore size 2.5 μm) filter papers.

Heavy metal concentrations in soils were determined by ICP-OES (Vista PRO, Varian, USA) following acidic digestion; soils (0.5 g, <2 mm) were digested with *aqua regia* (10 mL) using a block digester (OD-98-001, ODLAB, Korea). Each batch of digested soil samples included a certified reference material (Montana Soil SRM2711, National Institute of Standards and Technology) and blanks as quality control samples to validate the digestion. The digested soil suspensions were filtered through 0.45 μm disposable filters and trace metal concentrations in the filtrate determined using ICP-OES (8300DV, Perkin-Elmer, USA).

The phytoavailable metal pool was determined using 0.01 M $Ca(NO_3)_2$ (Seo et al., 2013). The derived transfer functions were primarily aimed at practical use in the field, and hence only in-situ desorption measurements using 0.01 M $Ca(NO_3)_2$ extraction were used for the derivation data set. Soil (10 g, <2 mm) was shaken for 2 h in an end-over-end shaker with 25 mL of 0.01 M $Ca(NO_3)_2$ in a 50 mL centrifuge tube. The soil suspension was filtered through 0.45 μm disposable filters and the trace metal concentrations in the filtrate analyzed using either ICP-OES or ICP-MS when concentrations were below the detection limit of ICP-OES. Given the strong positive correlations between extractable metals and plant metal contents, various neutral salt solutions have been proposed to determine chemical-based phytoavailable metal concentrations in soil. Representative solutions have included 1 M NH_4NO_3 (DIN, 1995), 1 M NH_4Cl (Krishnamurti et al., 1995), 0.1 M $NaNO_3$ (Gupta

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