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Derivation of reliable empirical models describing lead transfer from metal-polluted soils to radish (*Raphanus sativa* L.): Determining factors and soil criteria

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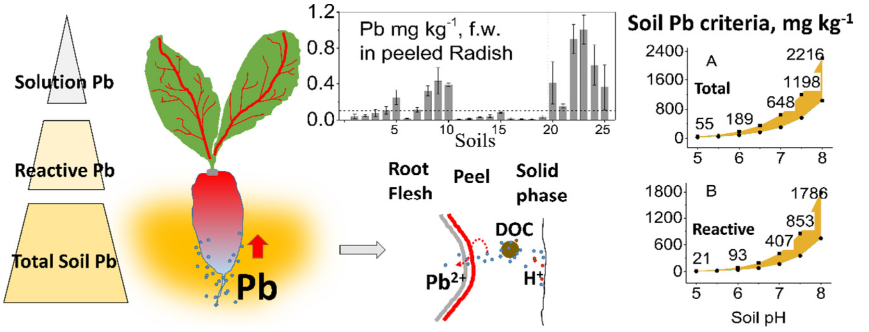
HIGHLIGHTS

- Soil pH and especially DOC control the bioavailability of Pb in soil solution.
- Free Pb^{2+} activities control Pb uptake in radish root tissues.
- $CaCl_2$ (0.01 M) extractable Pb is not consistent with soil solution Pb.
- CEC and pH are essential for deriving reliable uptake models using reactive Pb.
- Soil criterion for total Pb, $CaCl_2$ and HNO_3 extractable Pb are derived.

GRAPHICAL ABSTRACT



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ABSTRACT

Reliable models describing Pb transfer from soils to food crops are useful in the improvement of soil protection guidelines. This study provides mechanistic insights from in-situ soil solution measurement on the Pb uptake in the root tissues (RF) of radish, grown in 25 representative Pb-contaminated agricultural soils. Lead speciation and regression analysis indicate that >88.6% of the variation in RF Pb is attributable to free Pb^{2+} activity (aPb^{2+}) in the soil solution, which is predominantly controlled by pH and DOC. Higher DOC would increase the total dissolved Pb (C_{Sol}-Pb) in the soil solution but reduce the bioavailability of Pb to radish. C_{Sol}-Pb performs poorly in predicting RF Pb unless pH and DOC are included. However, 0.01 M $CaCl_2$ extractable Pb (C_{CC}-Pb) alone can satisfactorily predict RF Pb, attributable to the fact that C_{CC}-Pb is consistent with aPb^{2+}. C_{CC}-Pb can be predicted using C_{Sol}-Pb and pH. Total soil Pb (C_T-Pb), or 0.43 M HNO_3 extractable Pb (C_{NA}-Pb) has a strong, non-linear correlation with C_{Sol}-Pb or C_{CC}-Pb and it is therefore not surprising that C_T-Pb or C_{NA}-Pb, together with pH and CEC, can also satisfactorily predict RF Pb. Derived models are effective in identification of soils where RF Pb exceeds the food quality standard (FQS). Soil Pb criteria based on C_T-Pb, C_{NA}-Pb and C_{CC}-Pb are derived by inverse use of empirical models. The derived Pb criterion (target value) based on C_{CC}-Pb is 0.02 mg kg^{-1} and the stricter criterion (safe value) is 0.01 mg kg^{-1}, which allows a 5% probability for RF Pb to exceed FQS. Safe values based on C_T-Pb and C_{NA}-Pb ranged from 26 to 1036 mg kg^{-1} and 9 to 745 mg kg^{-1}, respectively.

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1. Introduction

Food crops can accumulate excessive lead (Pb) from Pb-contaminated agricultural soils and this can result in important risks to the human food chain (Bi et al., 2006; Cai et al., 2009; McGrath and Zhao, 2015). Reliable empirical models describing Pb transfer from soils to food crops can effectively identify those soils that are not safe for growing food crops and determine the extent to which soil remediation is required to ensure food safety, and thus are useful to improve soil protection guidelines (Rodrigues et al., 2012). However, reliable transfer models for Pb have barely been derived under field conditions (Attanayake et al., 2014; Bacigalupo and Hale, 2011; De Vries et al., 2007; McGrath and Zhao, 2015), because of the insufficient consideration of Pb bioavailability and other factors that can mask actual soil-plant relationships in respect of Pb.

Lead bioavailability and uptake by plants are controlled by soil conditions and plant physiology (Kim et al., 2010; Zhang et al., 2016b). Plant roots absorb Pb^{2+} ions from the soil solution. Depletion of Pb^{2+} in the rhizosphere is negligible if the re-supply of Pb^{2+} ions is faster than root adsorption/absorption. Equilibrated Pb^{2+} ion activity (aPb^{2+}) may then predominantly control Pb uptake. Mechanistic uptake models such as the free ion activity model (FIAM) and biotic ligand model (BLM) are often applicable. If Pb^{2+} depletion is substantial in the rhizosphere, Pb uptake is controlled by the slow re-supply process. A single extraction of aPb^{2+} at one point in time may therefore not reflect the kinetic uptake process. However, in most Pb-contaminated soils that are of concern regarding the safety of agricultural produce, total dissolved Pb (C_{Sol}-Pb) or aPb^{2+} is generally sufficient for Pb uptake by food crops. If aPb^{2+} can be predicted by the total dissolved Pb in the soil solution (C_{Sol}-Pb) and solution properties that influence Pb speciation, root Pb can then also be predicted by C_{Sol}-Pb. This is the basis of bioavailability-based approaches such as chemical extractions that are widely used to estimate the plant-available Pb for predicting Pb uptake in plants. However, the mechanistic insights of applying these approaches to predict Pb uptake, and influencing factors that control Pb bioavailability in soils are not sufficiently understood, especially under field conditions.

Soil pH, cation exchange capacity (CEC) and soil organic matter (OM) are factors known to influence Pb bioavailability in soils (Houben et al., 2013; McBride et al., 2004). Earlier studies indicate that aPb^{2+} or other metals can be predicted by geochemically active Pb (i.e., extracted with 0.43 M HNO_3) and bulk soil properties (Lofts and Tipping, 2011; McBride et al., 1997; Pampura et al., 2007; Sauvé et al., 1998). For instance, the WHAM/Model has been used successfully and validated in field conditions (Lofts and Tipping, 2011), and MINTEQ software is also widely used to similate the speciation of metals in the soil solution (Gustafsson, 2015). However, mechanistic models such as WHAM required many parameters and this may restrict their application. Moreover, plant-induced changes in pH and DOC can significantly influence aPb^{2+}, which may not be consistent with that of the bulk soil. However, plant-induced changes in Pb bioavailability are often neglected. Consequently, even aPb^{2+} can be difficult to use to predict Pb uptake by plants. In addition, other factors such as aerial Pb contamination (Schreck et al., 2012; Shahid et al., 2016; Sharma et al., 2008) and surface contamination of samples (McBride et al., 2014; Murray et al., 2011; Nabulo et al., 2012; Zhao et al., 2004) can virtually obscure Pb soil-plant relationships.

Radish (*Raphanus sativa* L.) was selected in the present study because exceedance of Pb limits is more common in radish roots than in leafy vegetables (Calderon and Billedo, 2014); aerial Pb contributes little to the underground tuber (De Temmerman et al., 2012; Xu et al., 2015), and surface contamination can also be removed by peeling the samples. The study aimed to (1) investigate mechanistic insights from in-situ soil solution measurements on Pb uptake by the root tissues (RF) of radish grown in 25 representative Pb-contaminated arable soils, (2) examine the basis of using different soil extract solutions to predict Pb uptake, (3) derive reliable models, using different Pb pools in soils and pertinent soil/solution properties and (4) derive soil criteria for Pb inversely using the derived empirical models, based on food quality standards.

2. Materials and methods

2.1. Description of the study region

Hezhang County (26° 46′–27° 28′N, 104° 10′–105° 03′ E), lies on the Guizhou plateau in south China at an average altitude of 1996 m. There is no plain in the study region, and almost all of the sporadically distributed farmland consists of sloping-field. Hezhang County still has 7.818 million tonnes of lead-zinc reserves. By 2000, there were >1000 smelting sites with records, some of which can be traced back to the 17th century (Bi et al., 2006; Yang et al., 2003). The indigenous zinc smelting activities ceased before 2006. However, agricultural soils (0–50 cm) accumulated considerable loadings of heavy metals due to historical long-term continuous input of smelting wastes (Bi et al., 2006). >20,000,000 t of smelting wastes were produced and contaminated the agricultural soils in Hezhang County. Earlier studies report that the total Pb content in agricultural soils ranged from 37 to 30,000 mg kg^{-1} (Yang et al., 2003). High concentrations of potentially toxic metals such as Cd and Pb have also been found in local agricultural produce (He et al., 2013; Zhang et al., 2016c).

2.2. Soil characteristics

A total of 25 agricultural soils were collected to a depth of 20 cm from long-term contaminated agricultural areas. Grid sampling (3 m × 3 m) and a portable X-ray fluorescence analyzer were used to ensure the representativeness of the samples collected, which represented all the major soil types in the study region, with a wide range of soil properties and Pb contamination levels. The method of soil pretreatment has been described by Zhang et al. (2016b). Soil clay content (vol%, <2 μm) was determined using a Model LS 13320 laser diffraction particle size analyzer (Beckman Coulter, Brea, CA). Soil organic matter content (OM) was determined using the acid dichromate oxidation method (Yeomans and Bremner, 1988). Cation exchange capacity (CEC) was determined using sodium acetate method (Lu, 2000). Soil pH, measured at a 1:2.5 (*w*/*v*) ratio of soil to 0.01 M $CaCl_2$ solution, averaged 7.3 and ranged from 4.6 to 7.9. However, the soil solution pH was relatively higher, averaging 7.7 and ranging from 6.2 to 8.3. The higher pH values were largely attributable to plant-induced changes in the soil solution which was extracted with in-situ soil moisture samplers during radish growth. CEC averaged 20.1 cmol(+) kg^{-1} (range 11.3–36 cmol(+) kg^{-1}). OM contents averaged 5.6% and ranged from 1.7% to 21%. Total soil Pb averaged 1294 mg kg^{-1} (range 57–6103 mg kg^{-1}. The statistical summary data respecting the physiochemical properties of soils sampled are presented in Table 1 and the detailed information is listed in Table A.1.

2.3. Soil extractions

Both weak and strong soil extracts were selected based on the hypothesis that plant roots absorb Pb ions directly from the soil solution, in which the dissolved Pb and some weakly adsorbed Pb are directly available to the roots during the period of plant growth. In-situ soil moisture samplers (Rhizosphere Research Products, Wageningen, The Netherlands) have been widely used for reliable sampling of various dissolved components such as trace metals and DOC in the soil solution (Knight et al., 1998; Sauvé et al., 2000). Furthermore, $CaCl_2$ (0.01 M) simulates the ionic strength of the soil solution and is widely used to extract the readily bioavailable metals from soils (Houba et al., 2000). Thus, the in-situ soil moisture sampling technique and $CaCl_2$ (0.01 M) extraction were adopted to represent weak extractions and short-term plant-available Pb. Extraction with a dilute nitric acid (0.43 M