Speciation and reactivity of lead and zinc in heavily and poorly contaminated soils: Stable isotope dilution, chemical extraction and model views[☆]

Zong-ling Ren [a, b], Yann Sivry [b], Mickaël Tharaud [b], Laure Cordier [b], Yongtao Li [a], Jun Dai [a, *], Marc F. Benedetti [b, **]

[a] Department of Soil Science, College of Resources and Environment, South China Agricultural University, Guangzhou 510642, China
[b] Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154, CNRS, 1 rue Jussieu, 75005 Paris, France

ARTICLE INFO

ABSTRACT

Correct characterization of metal speciation and reactivity is a prerequisite for the risk assessment and remedial activity management of contaminated soil. To better understand the intrinsic reactivity of Pb and Zn, nine heavily and poorly contaminated soils were investigated using the combined approaches of chemical extractions, multi-element stable isotopic dilution (ID) method, and multi-surface modelling. The ID results show that 0.1–38% of total Pb and 3–45% of total Zn in the studied soils are isotopically exchangeable after a 3-day equilibration. The intercomparison between experimental and modelling results evidences that single extraction with 0.43 M HNO_3 solubilizes part of non-isotopically exchangeable fraction of Pb and Zn in the studied soils, and cannot be used as a surrogate for ID to assess labile Pb and Zn pools in soil. Both selective sequential extraction (SSE) and modelling reveal that Mn oxides are the predominant sorption surface for Pb in the studied soils; while Zn is predicted to be mainly associated with soil organic matter in the soil with low pH and Fe/Mn oxides in the soils with high pH. Multi-surface modelling can provide a reasonable prediction of Pb and Zn adsorption onto different soil constituents for the most of the studied soils. The modelling could be a promising tool to decipher the underlying mechanism that controls metal reactivity in soil, but the submodel for Mn oxides should be incorporated and the model parameters, especially for the 2-pK diffuse layer model for Mn oxides, should be updated in the further studies.

© 2017 Published by Elsevier Ltd.

1. Introduction

Soil contamination by lead (Pb) and zinc (Zn) is widespread due to their extensive use in industrial, urban, and agricultural applications, posing risks to human and ecosystem health (Wuana and Okieimen, 2011). The two elements often occur together in metal contaminated ecosystems since they are frequently accompanied in metal ores (Böhmer and Kucera, 1986). However, they have different affinities with sorption sites of organic and mineral phases in the geosphere, thereby distributing into different chemical forms and exhibiting varying availability, mobility, and toxicity (Manceau et al., 2004; Appel et al., 2008).

Pb is strongly immobilized in soil by sorption to soil constituents (organic matter, oxides, and clay minerals) and formation of highly insoluble phosphates or sulphates (Morin et al., 1999; Villalobos et al., 2005; Degryse et al., 2007). Moreover, many studies have demonstrated that Pb is preferentially adsorbed onto manganese oxides (Bradl, 2004; Villalobos et al., 2005; Schneider et al., 2016). Morin et al. (1999) found that Pb^{2+} sorbed on hydrous iron oxides and manganese oxides represented more than 50% of the total Pb in mine tailings and smelter-contaminated soils from various geochemical systems. Organic matter was evidenced to be the main sink for Pb in the organic rich smelter-contaminated soil by using extended X-ray absorption fine structure (EXAFS) spectroscopy in conjunction with chemical separation techniques (Morin et al., 1999). Atkinson et al. (2011) compared Pb speciation in four soils contaminated with contrasting Pb sources assessed by sequential

extractions and stable isotopic dilution (ID). Their results showed that the isotopically exchangeable pool of Pb in the studied soils varied with Pb sources, and in the two mineral soils part of the so-called 'carbonate-bound' and 'Fe/Mn oxide-bound' Pb was not labile.

In contrast, the existing forms of Zn in soil are more variable for at least two reasons. First, Zn has versatile tetrahedral and octahedral coordination chemistry due to its lack of crystal field stabilization energy in either coordination. Second, the similarity in the effective ionic radius of Zn^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, and Al^{3+} allows its incorporation in a large number of soil minerals (Manceau et al., 2004, 2005). Jacquat and co-workers (Jacquat et al., 2008, 2009; Degryse et al., 2011) investigated Zn speciation in contaminated soils, which covered a wide range in soil properties, by combining XAFS spectroscopy, sequential extractions, and stable ID. They demonstrated that soil pH and total Zn concentration in soil are the most important factors controlling pedogenic Zn speciation (Jacquat et al., 2009). They also observed that the sum of Zn sorbed onto organic matter and hydroxides (i.e., tetrahedrally and octahedrally coordinated 'sorbed Zn') identified by XAFS or the first two/three fractions determined by selective sequential extraction (SSE) agreed reasonably well with the isotopically exchangeable fraction (Degryse et al., 2011).

To date, more comparative studies have been performed combining analytical techniques, such as 'SSE + ID' (Ahnstrom and Parker, 2001; Atkinson et al., 2011; Marzouk et al., 2013a) and 'SSE/ID + EXAFS' (Diesing et al., 2008; Degryse et al., 2011), to better interpret the metal speciation and reactivity in soil. In addition, in few studies a complementary tool, mechanistic multi-surface modelling was used to validate the metal distribution among the soil constituents against the analytical results and to relate the operational defined speciation that refers to the fraction extracted by chemical reagent to the classical speciation that refers to specific chemical compounds or oxidation states of elements calculated by the model. In those studies, the modelling results were compared with the results of SSE (Cui and Weng, 2015) and EXAFS (Cancès et al., 2003; Benedetti, 2006; Schneider et al., 2016), showing that the model can describe the interactions of metal ions with different sorption phases, such as organic matter, clay, iron and manganese oxides; and it often adequately predicted Cd, Cu, and Zn speciation in soil, but poorly for Pb (Cui and Weng, 2015; Ren et al., 2015a).

The objectives of this work were to (i) determine the Pb and Zn speciation and reactivity in nine poorly and heavily contaminated soils with chemical extractions (0.43 M HNO_3 extraction and 8-step SSE) and multi-element stable ID; (ii) find which of the soil components (organic matter, clay, iron hydroxides, and manganese hydroxides) is controlling Pb and Zn geochemistry with the help of multi-surface model; (iii) reveal the underlying action of each chemical protocol by comparing with modelling results.

2. Materials and methods

2.1. Soil samples

Soil UMT31 and CAD were collected from Aquitaine, France, representing Pb and Zn non-contaminated soils. Samples MOR, K6-1, and N14-1 contained increasing levels of Zn due to atmospheric fallouts from a former Zn-smelter plant in Nord-Pas-de-Calais, France, and N14-1 was also moderately contaminated in Pb. Soil FG, DBS, LC, and GJ were contaminated both in Pb and Zn due to the mining activities in South China. FG and DBS represented low contaminated soils, while LC and GJ represented moderately and heavily contaminated soil, respectively. The detailed sampling and chemical procedures, the soil mineralogical and physicochemical properties (pH, clay content, total organic carbon (TOC), carbonate-C, cation exchange capacity (CEC), amorphous iron oxides (Amor-Fe), crystalline iron oxides (Cry-Fe), manganese oxides, and total metal concentrations) are detailed in Ren et al. (2015a). The soils cover a wide range in pH (4.5–7.8), organic matter content (1.2–7.3%), clay content (6.7–67.1%), and total metal concentrations (23.6–2378 mg kg^{-1} and 42.3–2284 mg kg^{-1} for Pb and Zn, respectively) (Table A1).

2.2. Chemical extractions

Single extraction with 0.43 M HNO_3 was performed in triplicates at a ratio of 1 g air-dried soil to 10 mL of extractant for 2 h at room temperature by end-over-end shaking (Tipping et al., 2003). The soil suspensions were then filtered with 0.2 μm membranes and stored in vials at 4 °C prior to ICP-AES (Thermo Fischer iCAP 6200 Duo) analysis.

A modified eight-step SSE established by Quantin et al. (2002) was performed with a soil: solution ratio of 1.5/50 (g/mL) (Table A2). The detailed procedures and the analysis are described in Ren et al. (2015a). In short, this method partitioned the heavy metals into eight operationally defined chemical fractions: water soluble (F1: SOLU), exchangeable (F2: EXCH), acid-soluble (F3: ACI), bound to Mn oxides (F4: MNOX), bound to amorphous Fe and Al oxides (F5: FEOX1), bound to well crystalline Fe and Al oxides (F6: FEOX2), bound to oxidizable compounds (F7: OXID), and residual (F8: RES). The fractions extracted in the first steps can be regarded as the active fractions that are easily soluble, whereas the metals extracted in the other reduction/oxidization steps are less active and less available.

2.3. Stable isotopic dilution

Isotopically exchangeable pools at equilibrium time t (E_t values) were determined according to Sivry et al. (2011). Enriched stable isotope ^{204}Pb (isotopic abundance 99.94%) was purchased from ISOFLEX USA as metal foil which was dissolved in 5% HNO_3 to obtain a stock solution with a concentration of 522 mg L^{-1}, and a ^{67}Zn (isotopic abundance 94.60%) stock solution was supplied by SPECTRASCAN with a concentration of 10 mg L^{-1} in a 2.5% HNO_3 matrix. The preparation of the multi-element spiking solution of ^{204}Pb and ^{67}Zn for each soil follows the same procedure as that of ^{106}Cd and ^{65}Cu in the previous work of Ren et al. (2015a). The final amounts of ^{204}Pb and ^{67}Zn added into each soil (Table 1) were intended to be equal to or less than the amounts of the total dissolved metal concentration measured by the soil column–Donnan membrane technique (SC–DMT) using 0.002 M $Ca(NO_3)_2$ as background electrolyte at a soil: solution ratio of 100 g L^{-1} (Table A3) (Ren et al., 2015b).

The procedures of multi-element isotopic dilution for ^{204}Pb and ^{67}Zn are substantially the same with that for ^{106}Cd and ^{65}Cu (Ren

Table 1
Final spiking concentrations for each soil sample.

Sample	Pb (μg kg^{-1} soil)	Zn (μg kg^{-1} soil)
UMT31	1.0	12.3
CAD	12.9	274.7
MOR	9.1	993.0
N14-1	52.2	1088.6
K6-1	1.0	96.3
FG	812.0	1141.1
DBS	847.0	274.1
LC	55.3	28.3
GJ	3.1	86.7