



Evaluating specificity of sequential extraction for chemical forms of lead in artificially-contaminated and field-contaminated soils

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ABSTRACT

In the present study, we evaluated a commonly employed modified Bureau Communautaire de Référence (BCR test) 3-step sequential extraction procedure for its ability to distinguish forms of solid-phase Pb in soils with different sources and histories of contamination. When the modified BCR test was applied to mineral soils spiked with three forms of Pb (pyromorphite, hydrocerussite and nitrate salt), the added Pb was highly susceptible to dissolution in the operationally-defined “reducible” or “oxide” fraction regardless of form. When three different materials (mineral soil, organic soil and goethite) were spiked with soluble Pb nitrate, the BCR sequential extraction profiles revealed that soil organic matter was capable of retaining Pb in more stable and acid-resistant forms than silicate clay minerals or goethite. However, the BCR sequential extraction for field-collected soils with known and different sources of Pb contamination was not sufficiently discriminatory in the dissolution of soil Pb phases to allow soil Pb forms to be “fingerprinted” by this method.

It is concluded that standard sequential extraction procedures are probably not very useful in predicting lability and bioavailability of Pb in contaminated soils.

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1. Introduction

Lead has accumulated in soils of industrial countries over several centuries through anthropogenic processes such as atmospheric deposition from leaded gasoline, coal and oil combustion, incinerator emissions and mining and smelting activities [1,2]. The speciation of Pb in the soil solid phase is likely to control the potential bioavailability and toxicity of Pb to animals and humans, so much effort has been devoted to describing Pb speciation in soils, particularly using sequential extraction techniques [3]. Solubility of Pb in non-acid soils is typically very low as the metal forms insoluble oxide, hydroxide, carbonate and phosphate minerals, and binds strongly to iron oxide minerals and soil organic matter [4,5]. It is perhaps surprising that the reactivity or “lability” of soil Pb as measured using isotopic exchangeability is quite high [3].

Given the range of chemical forms that Pb can take in soils, it is important to determine whether commonly employed sequential extraction techniques are sufficiently selective to distinguish forms of Pb with different chemical labilities and bioavailability. Some studies suggest that plant availability of Pb is correlated to particular

Pb fractions extracted in the sequential extraction procedure [6]. However, previous research has shown that the bulk of Pb in contaminated soils is extracted in the “reducible” or “oxide” fraction, a strongly acidic extractant (pH near 2) of the 4-step BCR method [7,8]. Since Pb oxides, hydroxides and carbonates are common minerals of highly Pb-contaminated soils [5,9], and these minerals are quite susceptible to acid dissolution, it is very likely that the sequential extraction step, intended to dissolve Pb bound to oxides of Fe and Mn by reduction at pH 2 (the “reducible” fraction), would also dissolve a large fraction of Pb in these acid-labile minerals. In fact, the non-selectivity of reagents used in sequential extraction has been demonstrated previously [8,10]. For example, Atkinson et al. noted that non-labile Pb (as measured by isotope exchange) is extracted in the “reducible” and “carbonate” fractions as defined by sequential extraction [3]. Ahnstrom and Parker concluded that there was a poor correspondence between the size of the various fractions of Cd extracted by sequential extraction and the size of the labile Cd pool as measured using isotopic exchange [11]. In summary, there is considerable uncertainty about the value of standard sequential extraction procedures in predicting the lability and bioavailability of trace metals such as Pb and Cd in soils.

In the present study, we evaluate a commonly employed 3-step sequential extraction procedure (modified BCR test) for its ability to discriminate among several well-defined solid phases of Pb to determine whether sequential extraction can provide

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useful information on Pb speciation in soils. We further apply the BCR test to soils contaminated in the field by different sources of Pb in order to assess the ability of this sequential extraction to “fingerprint” soils by the type of Pb contamination.

2. Material and method

2.1. Preparation of minerals

In order to create solid forms of Pb with different inherent chemical liabilities as models for forms of Pb found in contaminated soils, we synthesized the pure Pb minerals, pyromorphite and hydrocerussite, both of which occur in Pb-contaminated soils, but have different susceptibilities to acid dissolution. We also synthesized microcrystalline goethite (FeOOH) to serve as a model mineral for strongly chemisorbed Pb. Pyromorphite and hydrocerussite were prepared according to the procedures described by Gebeyehu and Bostrom [12] and Flis et al. [13], and goethite synthesis was done according to Atkinson et al. [14]. Following synthesis, all mineral suspensions were repeatedly washed in deionized water to remove excess salts, then air-dried to powder form. X-ray diffraction was used to confirm the identity of the prepared minerals, with degree of crystallinity estimated from diffraction linewidths using the Debye–Scherrer equation.

2.2. Preparation of Pb-spiked soils and FeOOH

A 1000 mg l⁻¹ Pb stock solution was prepared by dissolving 1.599 g Pb(NO₃)₂ in distilled water and diluting to 1 l in a volumetric flask. A sandy loam topsoil (Arkport series) collected from a pasture (Ithaca, NY), and a peat soil sampled from a vegetable farm (Orange County, NY) were used as representative mineral soil and organic soil for Pb spiking. After air-drying the soil samples, they were pulverized and passed through a 2 mm sieve prior to further analysis. The Arkport mineral soil had a pH of 5.1, organic matter content of 31.8 g kg⁻¹ and total Pb content of 4.5 mg kg⁻¹ determined by a microwave-assisted hydrofluoric acid digestion technique (EPA 3052). The peat had a pH of 4.9, organic matter content of 711 g kg⁻¹ and total Pb content of 9.3 mg kg⁻¹ [15]. Organic matter content was determined using the Walkley–Black method.

Table 1
Pb-spiked solids prepared for aging and sequential extraction.

Spiked solid	ID	Total Pb (mg kg ⁻¹)
Mineral soil + pyromorphite	A+PM	1265 ± 57
Mineral soil + hydrocerussite	A+HC	1235 ± 212
Mineral soil + Pb(NO ₃) ₂	A+Pb	1146 ± 139
Peat + Pb(NO ₃) ₂	P+Pb	1124 ± 14
Goethite + Pb(NO ₃) ₂	G+Pb	1232 ± 56

Table 2
Modified BCR three-step sequential extraction procedure.

Extraction step	Fraction ID	Reagent used	Pb form targeted
1	A	Acetic acid CH ₃ COOH (0.11 mol l ⁻¹), pH 2.55	Exchangeable, water and weak acid-soluble Pb (e.g. carbonates)
2	B	Hydroxyl ammonium chloride NH ₂ OH · HCl (0.5 mol l ⁻¹), pH 1.54	Pb bound to reducible minerals (e.g. iron/manganese oxides)
3	C	Hydrogen peroxide H ₂ O ₂ (8.8 mol l ⁻¹), pH 2.45. Ammonium acetate CH ₃ COONH ₄ (1 mol l ⁻¹), pH 2.0	Pb bound to oxidizable solids (e.g. organic matter and sulfides)
4	D	Acid digestion (to determine unextracted Pb)	Residual Pb (occluded, structural)

In order to spike the soils and goethite with 1000 mg kg⁻¹ Pb in soluble form, we added 1.0 ml Pb (NO₃)₂ to each gram of dry mineral soil, organic soil and FeOOH along with a small volume of deionized water, shook the suspensions for 24 h, then centrifuged for 30 min at 5500 rpm. The supernatants were then discarded, and the solids were washed once with deionized water before being aged (in a moist state) in the laboratory at room temperature. Spiking of the mineral soil (MS) with the Pb minerals, pyromorphite and hydrocerussite, was done to achieve a final soil concentration close to 1000 mg kg⁻¹. This involved mixing 0.0665 g pyromorphite or 0.0625 g hydrocerussite with 50 g air-dry soil. These Pb mineral-spiked soils were stored in the air-dry state.

2.3. Aging and sequential extraction of Pb-spiked samples

The Pb-spiked samples prepared in this experiment are listed in Table 1, which shows three materials (mineral soil, organic soil and goethite) spiked with soluble Pb nitrate, and the mineral soil spiked with insoluble Pb hydroxycarbonate and phosphate. The total Pb concentrations in these materials, reported in Table 1, were determined by digestion using aqua regia and analysis of digests for Pb by flame atomic absorption.

Once the spiked materials listed in Table 1 were prepared, they were allowed to age and subsamples were collected for sequential extraction at 1 day, 1 week, 3 weeks, and 6 weeks after spiking with Pb. The modified 3-step BCR sequential extraction procedure, with extracting solutions used for each step, is shown in Table 2 [16]. The H₂O₂ and NH₂OH · HCl extractants were prepared on the same day the extraction was carried out because of the possibility of reagent decomposition. The fourth step listed in Table 2, involving acid digestion of the soil residue to determine the amount of total soil Pb not extractable in the 3-step process, was not carried out. Instead, total Pb was measured in the spiked materials as a less error-prone means of estimating the fraction of total Pb extracted by the 3-step procedure.

2.4. Sequential extraction of field-contaminated soils

We collected 6 contaminated soils with different sources of Pb contamination inferred from the history of the sites. These are listed in Table 3 and include soils from an industrial site (LP44), an old apple orchard (G6), an urban backyard (AL), and 3 soils from urban community gardens in New York City (GP, GA1, GA2). GA1 and GA2, although from the same garden, had different levels of Pb contamination and organic matter, possibly reflecting soil remediation of GA1 by compost amendment.

Key properties of the contaminated soils, specifically pH, organic matter content and total Pb concentration are summarized in Table 3. Soil pH (1:2.5 soil to water, w/v) was measured using a pH meter with glass electrode. Soil organic matter content was determined using the standard Walkley–Black dichromate oxidation method. Aqua regia digestion, based on the procedure

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