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Effect of aging on bioaccessibility of arsenic and lead in soils

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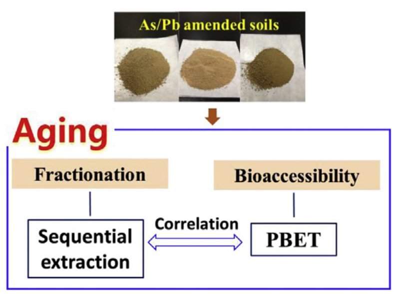
HIGHLIGHTS

- Aging effect on As/Pb bioaccessibility in soils was investigated using PBET assay.
- Non-specifically sorbed As attributed most to bioaccessibility.
- Carbonate and exchangeable Pb fractions contributed most to bioaccessible Pb.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of aging on the bioaccessibility of As and Pb in three soils spiked with As (40 or 400 mg kg^{-1}), Pb (150 or 1500 mg kg^{-1}) or As + Pb (40 mg kg^{-1} As and 150 mg kg^{-1} Pb) were investigated using the physiologically based extraction test (PBET). Prolonged aging in soils resulted in a decrease in As/Pb bioaccessibility, especially within the first month. After 76 weeks, As/Pb bioaccessibility in soils decreased to a stable level, with 48–84% and 8–34% for bioaccessible As and Pb respectively in the intestinal phase, illustrating that As in spiked soils was much more bioaccessible than Pb. Correlation analysis between sequential extraction data and PBET results showed that the non-specifically sorbed As contributed the most to bioaccessible As, while Pb bound with carbonates and exchangeable fractions were the source for bioaccessible Pb. For future work, minerals containing As and/or Pb instead of their soluble salts can be added to uncontaminated soils to better simulate the natural aging processes.

1. Introduction

In the last several decades various anthropogenic activities including mining, smelting and insecticide application have resulted in pollution of arsenic (As) and lead (Pb) in soils (Xenidis et al., 2010). U.S.EPA (2001) ranks As and Pb as the most common inorganic soil contaminants. Due to their negative effects on humans, especially with respect to their carcinogenetic and neurological

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effect on children (Tsuji et al., 2005; WHO, 2010), there is considerable concern regarding human exposure to soil As/Pb. Human exposure to As/Pb may occur via several pathways, but incidental soil ingestion is the main route, via principally hand-to-mouth activities for children (WHO, 2010; Moya and Phillips, 2014). After ingestion, soil As/Pb may be absorbed through the digestive tract and transferred to tissues throughout the body via the systemic circulation system (WHO, 2010).

Absorption of As/Pb following soil ingestion can be overestimated when predictions are based solely on total concentrations, as the actual As/Pb reaching systemic circulation depends on their solubility in soils and human nutritional status (Ryan et al., 2004; Abrahams, 2012). Contaminant bioavailability in soils may be determined using animal testing, but these assays are expensive and time consuming, so recent attention has been paid to develop *in vitro* tests, which can mimic the human digestion processes. Such tests estimate contaminant bioaccessibility, which is the fraction that is soluble in the gastrointestinal tracts and is available for absorption (Ruby et al., 1999; Juhasz et al., 2014). The physiologically based extraction test (PBET) is a popular *in vitro* test in metal bioaccessibility assessment (Markus and McBratney, 2001; Attanayake et al., 2014; Ren et al., 2015; Yin et al., 2015).

Bioaccessibility of As and Pb has been incorporated into human health risk assessments by U.S.EPA (U.S.EPA, 2002, 2007, 2011). These tests have recently been adopted and proved to be useful (Juhasz et al., 2014; Henry et al., 2015; Li et al., 2015a). Many studies have focused on the oral bioaccessibility and the exposure risk of metals in contaminated soils (Udovic and McBride, 2012; Defoe et al., 2014; Attanayake et al., 2015). However, the information on their bioaccessibility and exposure risk in amended soils during the aging process is limited. Reported research is related to the single As bioaccessibility in soils (Tang et al., 2007; Quazi et al., 2010, 2011).

After soluble As/Pb addition to soils, their bioaccessibility decreases with time, which is termed aging (Ma et al., 2006). During aging, the As/Pb partitioning process in soils affects and changes their available forms (Degryse et al., 2009). The partitioning process is related to soil properties and governed by different soil fractions (Tang et al., 2007; Hayes et al., 2012). Sequential extraction has been widely used to measure metal fractionation and bioaccessibility in soils (Tessier et al., 1979; Wenzel et al., 2001). The method identifies different pools of metals in soils with different availability and provides valuable information on metal bioaccessibility in soils (Sipos et al., 2008).

In this study, three different soils were spiked with different As and Pb levels. Changes in their bioaccessibility and human health risk with time in the soils were estimated using the PBET procedure and calculations of hazard quotient and carcinogenic risk were performed. The objectives were (1) to evaluate the aging effect on As and Pb bioaccessibility in different soils, and (2) to investigate the relationship between bioaccessible As/Pb and their fractionation in amended soils.

2. Materials and methods

2.1. Soil preparation and characterization

Surface soils (0–20 cm) with different pH were collected from Tianjin (TJ, pH 7.0), Lanzhou (LZ, pH 7.7) and Tai'an (TA, pH 5.7) in China. Details of the soils were described by Liang et al. (2014). Soil samples were air-dried, ground and sieved through a 2 mm mesh. Soil pH and cation exchange capacity (CEC) were measured using standard protocols (Sparks et al., 1996). Particle size of soils was analyzed using a laser diffractometer (Mastersizer 2000, Malvern, UK). Contents of total organic and inorganic carbon were determined using a total carbon analyzer (Vario TOC, Elementar, Germany). Amorphous and crystalline Fe oxides were measured following Sparks et al. (1996). The concentrations of Mn, Al, As and Pb in soils were determined by inductively coupled plasma mass spectrometry (ICP–MS, NexION 300X, PerkinElmer, USA) after soil digestion according to USEPA method 3050B. The analyses were carried out in triplicates and the results were presented as mean values.

Samples (1 kg, triplicates) from each soil were spiked with soluble As (Na_3AsO_4) or Pb ($Pb(NO_3)_2$) at different levels: (1) control, (2) 40 mg kg^{-1} As (As_{40}), (3) 400 mg kg^{-1} As (As_{400}), (4) 150 mg kg^{-1} Pb (Pb_{150}), (5) 1500 mg kg^{-1} Pb (Pb_{1500}), and (6) 40 mg kg^{-1} As + 150 mg kg^{-1} Pb (As_{40}+Pb_{150}). The lower spiked concentrations of As/Pb were comparable with the reported concentrations in contaminated agricultural soil in China (Cai et al., 2003; Liao et al., 2006), and the higher concentrations represented severe contamination and were similar to those used in previous studies on metal aging effect in soils (Tang et al., 2007; Quazi et al., 2010). The soils were then stored under constant moisture content (50% water holding capacity) in plastic bags, which opened partly to maintain aeration and kept in a dark at room temperature. Milli-Q water was added every two weeks based on water lose in the spiked soils, mimicking field drying–wetting cycles (Ma et al., 2006; Tang et al., 2007). Aliquots of soil samples were taken at different times (0, 1, 2, 4, 9, 17, 33 and 76 weeks) and then air-dried and ground gently with a mortar.

2.2. In vitro procedures

It is generally assumed that only fine soil particles adhering to children's hands are likely to be ingested (U.S.EPA, 2002). So soil fractions <0.25 mm was used for the *in vitro* test. Bioaccessibility of As and Pb was estimated using the physiologically based extraction test (PBET) (Ruby et al., 1996). Briefly, the test was conducted with 0.3 g soil in 30 mL of synthetic digestive solution in a 37 °C water bath in two phases: gastric phase (pH 2.5, 1 h) and intestinal phase (pH 7.0, 4 h). Solution pH was monitored constantly and adjusted with concentrated HCl or $NaHCO_3$ powder when necessary throughout the procedure. Continuous mixing was performed using a shaker at 100 rpm. After the gastric phase, the suspension sample was centrifuged at 2100 *g* for 25 min and then 3 mL supernatant was collected and filtered through 0.45 μm polysulfone filters. After that, the gastric solution was modified to the intestinal solution by compensating 3 mL gastric solution and adjusting the pH from 2.5 to 7.0 followed by the addition of bile salts and pancreatin. 3 mL sample from the intestinal phase was obtained after 4 h. All *in vitro* tests were performed in triplicate, and soluble As and Pb concentrations in the solutions were analyzed using ICP–MS.

Arsenic and lead bioaccessibility was calculated by dividing the gastric phase or intestinal phase extractable As/Pb by total soil As/Pb concentration (Eq. (1)),

$$\text{Bioaccessibility}\ (\%) = \frac{\text{in vitro As/Pb}}{\text{total As/Pb}} \times 100 \tag{1}$$

where, *in vitro* As/Pb means As/Pb (μg) extracted from soils following gastric or intestinal phase treatment and total As/Pb represents As/Pb (μg) present in contaminated soils.

2.3. Sequential extraction procedures

For As, an improved sequential extraction procedure by Wenzel et al. (2001) was used. There are five As fractions: non-specifically sorbed As (NS1, $(NH_4)_2SO_4$ extractable), specifically sorbed As (SS2,