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Modification of an existing in vitro method to predict relative bioavailable arsenic in soils

Shane Whitacre [a], Nicholas Basta [a, *], Brooke Stevens [b], Valerie Hanley [c], Richard Anderson [d], Kirk Scheckel [e]

[a] School of Environment and Natural Resources, The Ohio State University, Columbus, OH, United States
[b] Army Corps of Engineers Engineer Research and Development Center, Vicksburg, MS, United States
[c] Department of Toxic Substances Control, California EPA, Sacramento, CA, United States
[d] U.S. Air Force Center for Engineering and the Environment, Lackland AFB, TX, United States
[e] U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH, United States

HIGHLIGHTS

- The OSU-IVG often extracted less As in vitro than in vivo RBA As, in particularly for soils from historical gold mining.
- The CAB method, which is a modified OSU-IVG method extracted more As than OSU-IVG for most soils.
- The CAB method accurately predicts RBA As especially for low to moderately contaminated soils (<1,500 mg As/kg).

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ABSTRACT

The soil matrix can sequester arsenic (As) and reduces its exposure by soil ingestion. In vivo dosing studies and in vitro gastrointestinal (IVG) methods have been used to predict relative bioavailable (RBA) As. Originally, the Ohio State University (OSU-IVG) method predicted RBA As for soils exclusively from mining and smelting sites with a median of 5,636 mg As kg^{-1}. The objectives of the current study were to (i) evaluate the ability of the OSU-IVG method to predict RBA As for As contaminated soils with a wider range of As content and As contaminant sources, and (ii) evaluate a modified extraction procedure's ability to improve prediction of RBA As. In vitro bioaccessible (IVBA) by OSU-IVG and California Bioaccessibility Method (CAB) methods, RBA As, speciation, and properties of 33 As contaminated soils were determined. Total As ranged from 162 to 12,483 mg kg^{-1} with a median of 73 mg kg^{-1}. RBA As ranged from 1.30 to 60.0% and OSU-IVG IVBA As ranged from 0.80 to 52.3%. Arsenic speciation was predominantly As(V) adsorbed to hydrous ferric oxide (HFO) or iron (Fe), manganese (Mn), and aluminum (Al) oxides. The OSU-IVG often extracted significantly less As in vitro than in vivo RBA As, in particularly for soils from historical gold mining. The CAB method, which is a modified OSU-IVG method extracted more As than OSU-IVG for most soils, resulting in a more accurate predictor than OSU-IVG, especially for low to moderately contaminated soils (<1,500 mg As kg^{-1}) with RBA As = 0.81 IVBA As + 3.2, $r^2 = 0.91$.

1. Introduction

Exposure risk associated with soils contaminated with arsenic (As) is assessed by human health risk assessment (HHRA). A critical component of HHRA is exposure assessment by various exposure pathways. In soils, often the most important pathway for As, the risk driver, associated with human exposure is incidental soil ingestion. However, use of total soil As often overestimates exposure because physiochemical properties of the soil matrix can sequester As and reduces its transmission through exposure pathways. Currently, the recommended default relative bioavailability (RBA) for soil As is 60% (U.S. EPA, 2010).

A more accurate site-specific HHRA accounts for measured RBA of As in a soil matrix as part of the exposure assessment. Many sites

Abbreviations: GI, gastrointestinal; IVBA, in vitro bioaccessible; RBA, relative bioavailability; HHRA, human health risk assessment.

* Corresponding author. 410B Kottman Hall, 2021 Coffey Rd., Columbus, OH, 43210, United States.
E-mail address: basta.4@osu.edu (N. Basta).

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have soils with As bioavailability less than the default thus resulting in an over-estimation of risk. Applying site-specific bioavailability allows for a more accurate risk assessment and may reduce the need or extent of remediation. Appropriate animal models, similar to human gastrointestinal (GI) physiology, are often used to determine bioavailability of As in contaminated soil. The most commonly used animal model for determining RBA As is the juvenile swine model (Rodriguez and Basta, 1999; Basta et al., 2007; Rees et al., 2009). In addition to juvenile swine, monkeys (Freeman et al., 1995; Roberts et al., 2002, 2007), adult mouse (Bradham et al., 2011), and rabbit models (Freeman et al., 1993) have also been used. Use of animal models for determining RBA As has been reviewed by Basta and Juhasz (2014). Several disadvantages in conducting animal studies include expense, specialized facilities and personnel requirements, and time required to measure contaminant bioavailability.

In order to overcome some of the difficulties and expenses associated with animal dosing trials used to assess bioavailability of contaminants in soil, extensive research efforts have been directed toward development of in vitro methods that simulate the GI environment, to predict RBA As. While there are multiple efforts to advance development and adoption of an in vitro bioaccessibility (IVBA) method, the two approaches in the United States employ pH buffered and unbuffered extraction gastric fluids; a 0.4 M glycine buffered gastric solution at pH 1.5 (Juhasz et al., 2006, 2007a, 2007b, 2008; Bradham et al., 2011; Brattin et al., 2013; Diamond et al., 2016), and the OSU-IVG which consists of an unbuffered gastric solution at pH 1.8 followed by an unbuffered intestinal solution at pH 6.5 (Basta et al., 2007; Nagar et al., 2009; Juhasz et al., 2009; Li et al., 2015). The experimental conditions of many of the bioaccessibility methods are similar. The scope of the current study was to investigate the effect of soil As content and source on the ability of bioaccessibility to predict RBA As. However, it is beyond the scope of this study to investigate all bioaccessibility methods and have selected the OSU IVG method for evaluation.

The OSU-IVG was the first in vitro method to be correlated with swine RBA As (Rodriguez and Basta, 1999). Juvenile swine RBA As were determined using soil in a dosing vehicle of wet feed. The OSU-IVG method of Rodriguez and Basta, (1999) incorporated this dosing vehicle in the OSU-IVG method to determine bioaccessible As. Use of the dosing vehicle in the in vitro method was problematic because (i) the IVG method should be developed for fasting conditions, and (ii) obtaining the exact type of dosing vehicle is problematic making it difficult to standardize the method for use by others. In Basta et al. (2007), bioaccessible As was determined by OSU-IVG with and without the dosing vehicle. Basta et al. (2007) data for 10 soils was combined with IVBA As values for 4 soils (Basta et al., 2001) that did not use dosing vehicle to obtain the following linear regression to predict RBA As.

$$\%\text{RBA As} = 0.883\ (\%\text{OSU-IVG GE}) + 9.6,\ r^2 = 0.74 \quad (1)$$

The 14 soils used to produce Eqn. (1) were exclusively from mining and smelting sites with total As contents ranging from 405 to 17,500 mg As kg^{-1} with a median of 5,636 mg As kg^{-1}. In many cases, these As concentrations are much higher than many soils for which bioavailability adjustments would be considered and also much higher than the swine in vivo vs. in vitro correlations (IVIVC) developed for the 0.4 M glycine method reported by (Juhasz et al. (2009); median of 262 mg As kg^{-1}) and (Brattin et al. (2013), median of 385 mg As kg^{-1}). While it has been demonstrated that IVBA As by the OSU-IVG is not related to total As content (Whitacre et al., 2013), it is unknown how well the OSU-IVG method will measure and/or predict RBA over a wider concentration range of soils As, particularly lower As concentrations, and from As sources outside those used to develop the regression. The objectives of the current study were to (i) evaluate the ability of the OSU-IVG method to predict RBA As for As contaminated soils with a wider range of As content and As contaminant sources, and (ii) evaluate a modified extraction procedure's ability to improve prediction of RBA As.

2. Materials and methods

2.1. Study soils

Thirty-three As containing soils that represent a wide variety of As sources were selected for this study. Soil samples were homogenized and sieved to <250 μm. Total content of As and other elements were determined using microwave assisted acid digestion using a CEM Corporation Mars Express Microwave (U.S. EPA Method 3051a, U.S. EPA, 2007a) with subsequent analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Agilent 720 (U.S. EPA, 2007b). Reactive Fe was determined by the acid ammonium oxalate method of McKeague and Day (1966).

Other additional soil and solid waste analyses including soil pH, organic carbon, electrical conductivity, and soil texture have been reported previously (Basta et al., 2016). Arsenic speciation was determined from As X-ray absorption near-edge structure (XANES) spectra and the extended x-ray absorption fine structure (EXAFS). Linear combination, least-squares fitting provided quantitative determination of species relative abundance in samples containing multiple As or Fe species. Detailed procedures for arsenic speciation are described in Basta et al. (2016) and California DTSC (2015).

2.2. Determination of relative bioavailable arsenic

Juvenile swine bioassays were used to determine RBA As for the study soils according to Brattin and Casteel (2013). In short, soils were administered to a dose group at a known As levels for 15 days. Additionally, the study included a non-treated group to serve as a control for determining background arsenic levels as well as a sodium arsenate reference group. All doses were administered orally and As excreted in urine was used to determine RBA As for each soil. Further details of the bioassay and RBA derivation are described in Basta et al. (2016) and California DTSC (2015).

2.3. Determination of bioaccessible arsenic

In vitro laboratory methods were used to determine IVBA As. The two IVBA methods investigated were the OSU-IVG (Basta et al., 2007) and the California Arsenic Bioaccessibility Method (CAB, California DTSC, 2015). Bioaccessible As was determined from the gastric phase of both methods.

Bioaccessible As was determined by the OSU-IVG method as follows. The extraction solution consisted of 0.10 M NaCl and 1% porcine pepsin. The solution was heated in an open extraction vessel, in a 37° C hot water bath. When the solution reached 37° C, soil (1 g, < 250 μm) was added. The sample was thoroughly mixed with the solution using a paddle stirrer to maintain a homogenous suspension, and the pH is adjusted drop wise to 1.8 using 6 M trace metal grade HCl. The solution pH is continuously monitored and adjusted to 1.8 ± 0.1. After 1 h, 10 mL of gastric solution was removed for analysis. The extract was immediately centrifuged (11,160 g for 15 min) and then filtered (0.45 μm). The extracted As is expressed as IVBA as shown in eqn. (2).

$$\text{IVBA As}\ (\%) = [\text{bioaccessible As}\ (\text{mg kg}^{-1})]/[\text{3051a As}\ (\text{mg kg}^{-1})] \times 100 \quad (2)$$