Geoderma 152 (2009) 137–144

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Assessing the selectivity of extractant solutions for recovering labile arsenic associated with iron (hydr)oxides and sulfides in sediments

Cynthia J. Paul *, Robert G. Ford [1,2], Richard T. Wilkin [3,4]

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, United States

ARTICLE INFO

Article history:
Received 21 October 2008
Received in revised form 7 May 2009
Accepted 31 May 2009
Available online 30 June 2009

Keywords:
Arsenic
Iron
Sulfur
Sequential extraction

ABSTRACT

Sequential extractions can provide analytical constraints on the identification of mineral phases that control arsenic speciation in sediments. Model solids were used in this study to evaluate different solutions designed to extract arsenic from relatively labile solid phases. Sequential and single-step extractions were conducted to evaluate the selectivity of these extraction solutions for differentiating arsenic associated with iron (hydr) oxides and iron sulfides. Extraction phases were categorized as 1) $MgCl_2$-extractable, 2) phosphate-extractable, 3) ascorbate-extractable, and 4) HCl-extractable when the procedure is applied in sequence. Arsenic, iron, and sulfur concentrations were compared between the single-step and sequential extractions. Additionally, phosphate extractions were conducted at three pH values for comparison purposes. Application of the extraction protocol to orpiment of varying crystallinity and crystalline arsenopyrite indicated that these phases have limited solubility in the extractant solutions. Extraction with ascorbate at circumneutral pH appears to target dissolution of poorly crystalline iron (hydr)oxides and is largely selective for extracting arsenic associated with this phase. Tests of the ascorbate extraction solution on sediment samples previously characterized for mineralogy and solid phase arsenic speciation by X-ray absorption spectroscopy reveal the utility of ascorbate for differentiating arsenic associated with poorly crystalline iron (hydr)oxides and iron sulfides. Results from tests in which samples were dried by different approaches or were subjected to air exposure prior to or during extraction demonstrate the importance of sample handling on the outcome of extraction protocols.

1. Introduction

Arsenic contamination is widely distributed due to its natural origin as well as its historical industrial uses. Ground water contaminated with arsenic poses a significant health threat to the public due to its toxicity at low concentrations. In the United States, the federal maximum concentration level (MCL) for arsenic in drinking water has been lowered from 0.05 mg/L to 0.01 mg/L. Naturally occurring arsenic concentrations in ground water often exceed the MCL in parts of the western United States (Smedley and Kinniburgh, 2002), and large accumulations exist in some soils and sediments due to human activities (Durant et al., 1990; Davis et al., 1994). Sources of anthropogenic arsenic pollution include pesticide, herbicide and fertilizer production, glass and ceramic manufacturing industries, petroleum refining, and smelting of arsenic-bearing ores (Blakely, 1984; Smedley and Kinniburgh, 2002). The toxicity of arsenic varies according to its oxidation state. Arsenic is stable in four oxidation states (+5, +3, 0, −3) under Eh conditions occurring in natural water systems (Ferguson and Gavis, 1972). However, arsenite ($H_nAsO_3^{n-3}$) and arsenate ($H_nAsO_4^{n-4}$) species are the most common forms with arsenite displaying greater toxicity (Korte and Fernando, 1991). Both oxyanion species are more commonly found in natural environments than metallic arsenic (As(0)) and As(-III), which are only found in extremely low Eh environments (Rubel and Williams, 1980).

Under natural subsurface conditions, arsenic is subject to a variety of biogeochemical reactions that dictate its chemical speciation, oxidation state, and solid-solution partitioning (e.g., Pierce and Moore, 1982; Fuller et al., 1993; Dixit and Hering, 2003; Stollenwerk, 2003; Helz and Tossel, 2008). Processes that can remove arsenic from the solution phase include sorption onto clays and other minerals or sorption onto and co-precipitation with hydrous iron (hydr)oxides and iron sulfides. Arsenate is stable in aerobic water and may be removed by several mechanisms. It has been shown that arsenate co-precipitates with or strongly adsorbs onto hydrous iron (hydr)oxides. Site specific geochemical factors such as pH and redox conditions, abundance of Fe and Al oxides, and organic matter content can affect arsenic mobility and adsorption (U.S. EPA, 2007). The rate and extent

---

* Corresponding author. Tel.: +1 580 436 8556; fax: +1 580 436 8703.
E-mail addresses: paul.cindy@epa.gov (C.J. Paul), ford.robert@epa.gov (R.G. Ford), wilkin.rick@epa.gov (R.T. Wilkin).

[1] 26 West Martin Luther King Dr., Cincinnati, OH 45268, United States.

[2] Tel.: +1 513 569 7501.

[3] 919 Kerr Research Dr., Ada, OK 74820, United States.

[4] Tel.: +1 580 436 8874.

0016-7061/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.geoderma.2009.05.026

to which arsenic can be mobilized and released into ground water depend on chemical speciation and partitioning onto soils and sediments (Gruebel et al., 1988).

Various extraction methods (Tessier et al., 1979; Pickering, 1981; Huerta-Diaz and Morse, 1990; Keon et al., 2001; Wenzel et al., 2001) have been examined in order to estimate the partitioning of arsenic and other metals among various solid phases in sediments and soils. In this study, single-step and sequential extraction procedures were compared to evaluate arsenic partitioning onto poorly crystalline iron (hydr)oxides and sulfides with comparison to sediment samples collected from a contaminated site. Arsenic associated phases were categorized as 1) $MgCl_2$-extractable, 2) phosphate-extractable, 3) ascorbate-extractable and 4) HCl-extractable. Extraction behaviors of the iron (hydr)oxides are compared to arsenic-bearing sulfide minerals to examine potential overlaps of arsenic pools determined using chemical extractions when applied to materials containing complex mineral mixtures. Extracted arsenic content was compared between the single-step extractions and the sequential extractions. Additionally, single-step phosphate extractions were performed at three different pH values to evaluate the impact of pH on arsenic removal in this step. Extraction behavior for arsenic, iron and sulfide for sediments was also evaluated relative to independently measured speciation and mineralogical characteristics.

2. Experimental

2.1. Tested solids

2.1.1. Iron (hydr)oxides

Ferrihydrite (2-line) was within synthesized by titrating a solution of 1.5 M $FeCl_3$ with 2.0 M NaOH according to Schwertmann and Cornell (1991). The resultant precipitate was isolated by centrifugation and washed four times with deionized water. The separated precipitate was dried at 72 °C for 38.5 h and ground with a mortar and pestle to pass through a 250 µm sieve. Following sieving, arsenate was adsorbed onto the ferrihydrite [pH 10, As–Fh(ads)], as well as goethite [pH 5.3, As–FeOOH(ads); Alfa Aesar] and hematite [pH 5.8, As–Fe_2O_3 (ads); Connelly-GPM] (see Table 1 for amount of adsorbed arsenic). Arsenate was adsorbed to these solids by adding 35 mL of 2 mg/L As solution (from Na_2HAsO_4) to 45 mL polyethylene centrifuge tubes containing 0.1 g of iron (hydr)oxide; recovered solids with adsorbed As were not dried prior to extraction. Arsenate co-precipitated during ferrihydrite synthesis [As–Fh(cpt)] was formed by precipitating a solution containing 0.1 M $FeCl_3$, 0.0001 M Na_2HAsO_4, and 0.01 M HNO_3 by drop-wise titration to pH 5 with 2 M NaOH. The resultant precipitate was aged in solution at room temperature for approximately 14 h and then isolated by centrifugation. Separated solids were oven dried at 30 °C overnight (14 h) and ground with a mortar and pestle to pass through a 250 µm sieve.

2.1.2. Sulfides

A range of synthetic and natural sulfide minerals were subjected to extraction tests in order to evaluate potential selectivity in mixed-mineral systems encountered in natural environments. One set of sulfidic phases included arsenic-bearing minerals: arsenopyrite (FeAsS, Ninas de Panasqueira, Portugal; Ward's Scientific), orpiment (As_2S_3-nat, Manhattan, Nevada; Ward's Scientific), and poorly crystalline synthetic orpiment (As_2S_3-syn, 99.9%, Alfa Aesar). For the mineral specimens, large pieces of each were lightly crushed to pass through a 250 µm sieve. These solids (0.02 g each) were diluted with 1.98 g of ground and washed silica (<25 mm; Fisher scientific) prior to extraction. No precaution was taken to prevent oxygen exposure during handling and extraction for these solids. A second set of sulfidic phases included arsenic partitioned to mackinawite (FeS), which was prepared following the method described in Wilkin and Ford (2002). Equivalent volumes of 0.1 M $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Aldrich) and 0.1 M NaHS solutions were mixed and equilibrated at room temperature. All solutions were prepared from deoxygenated and distilled water. Sodium bisulfide solution was prepared by purging 0.1 M NaOH with a 10 vol.% hydrogen sulfide gas mixture (balance nitrogen). The suspension resulting after mixing the stock solutions was allowed to settle in a sealed glass vial placed in an anaerobic chamber. An aliquot of 1000 mg As(V) L^{-1} or 1000 mg As(III) L^{-1} prepared from $Na_2HAsO_4 \cdot 7H_2O$ or $NaAsO_2$, respectively, was added to the glass vial with a needle syringe through a rubber septum. The vial contents were shaken and allowed to equilibrate overnight. Solids were removed from the solution by filtration (0.2 µm Nucleopore) in an anaerobic chamber. Samples of FeS were handled in a Coy anaerobic chamber containing 2 to 5% (v/v) H_2, less than 1 ppmv O_2, with a N_2 balance. Characteristics of the model solids and sediment samples are shown in Table 1.

Table 1
Physical and chemical characteristics of the natural and synthesized model solids and sediments collected from the Industri-Plex Superfund Site (U.S. EPA, 2005).

	Surface area	Arsenic (As)	Iron (Fe)	Sulfur (S)
	m^3/g[a,b]	mg/kg[c]	mg/kg[c]	mg/kg[c]
Model solids				
As–Fh(cpt)	180	842	626,966	–
As–Fh(ads)	58.8	19,650	746,000	–
As–FeOOH(ads)	4.40	19,650	629,000	–
As–Fe_2O_3(ads)	5.10	14,680	699,000	–
As_2S_3-syn	4.60	609,000	–	391,000
As_2S_3-nat	1.30	609,000	–	391,000
FeAsS	NM	460,000	343,000	197,000
As(III)–FeS(ads)	NM	20,000	615,600	364,400
As(V)–FeS(ads)	NM	19,600	615,800	364,500
Contaminated sediments				
WI01-NEP	NM	830	77,000	1800
WI02	NM	630	245,693	4700
WI04	NM	840	263,000	3500
SC0401-1	NM	682	74,600	11,400
SC0401-3	NM	1680	119,000	109,500
SC0401-6	NM	1070	85,600	28,500
SC0401-7	NM	973	86,500	23,200
NC0901-1	NM	207	19,000	8300
NC0901-4b	NM	1490	70,400	56,800
NTW4	NM	1180	75,000	37,500

Reported values are measured for solids collected following preparation.

[a] Analyzed using Coulter SA-3100 surface area analyzer for the pure mineral, not the mixture with silica used in the extraction experiments.

[b] Analysis precision expected to be within 5%.

[c] Values for As, Fe, and S in the model solids were calculated based on stoichiometric relationships.

2.1.3. Contaminated sediments

Sediment samples from a hazardous waste site were subjected to extraction with ascorbate according to Step 3 below (Section 2.2). Sediments were collected from the Halls Brook Holding Area (HBHA) Pond located approximately 16 km northwest of downtown Boston, MA (USA). The pond receives discharge of ground water with elevated concentrations of arsenic, petroleum hydrocarbons, ferrous iron, and sulfate. Site details, sampling and preservation methods are described in U.S. EPA (2005), and chemical composition data are provided in Table 1. Except for samples WI01-NEP, WI02, and WI04, all sediment samples were handled in a manner to prevent exposure to oxygen during preparation and extraction; a split from sample NTW4 was allowed to oxidize prior to extraction to assess the impact on arsenic extraction.

2.2. Sequential extraction procedure

A summary of extraction conditions and order used for sequential extractions is shown in Table 2. All stock solutions were prepared using reagent grade chemicals and deionized water (Millipore® Milli-