

## Effect of experimentally induced reducing conditions on the mobility of arsenic from a mining soil

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Received 22 April 2004; received in revised form 11 March 2005; accepted 14 March 2005

Available online 28 April 2005

### Abstract

A method for estimating the release of contaminants from contaminated sites under reducing conditions is proposed. The ability of two chemical reducing agents, sodium ascorbate and sodium borohydride, to produce different redox environments in a gold mining soil contaminated with arsenic was investigated. Liquid–solid partitioning experiments were carried out in the presence of each of the reducing agents at different pH conditions. Both the effect of varying concentrations of the reducing agent and the effect of varying pH in the presence of a constant concentration of the reducing agent were studied. Concentrations of sodium ascorbate ranging from 0.0075 to 0.046 mol L<sup>-1</sup> and concentrations of sodium borohydride ranging from 0.0075 to 0.075 mol L<sup>-1</sup> were examined. The addition of varying concentrations of sodium borohydride provided greater reducing conditions (ranging from -500 to +140 mV versus NHE) than that obtained using sodium ascorbate (ranging from -7 to +345 mV versus NHE). The solubilization of arsenic and iron was significantly increased by the addition of sodium ascorbate for all concentrations examined and pH tested, compared to that obtained under oxidizing conditions (as much as three orders of magnitude and four orders of magnitude, respectively, for the addition of 0.046 mol L<sup>-1</sup> of sodium ascorbate). In contrast, the alkaline and highly reduced soil conditions obtained with sodium borohydride lead to a lower effect on arsenic solubilization (as much as one order of magnitude for pH values between ca. 7 and 10 and no effect for pH values between ca. 10 and 12) and no effect on iron solubilization for all concentrations examined and pH tested. At similar ORP–pH conditions the results of extraction for arsenic and iron were different for the two reagents used.

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*Keywords:* Arsenic; Reducing conditions; Contaminated soil; Leaching; Mobility

### 1. Introduction

Risk assessment of contaminated sites and determination of remediation endpoints require the determination of leaching potentials. Leaching tests are important laboratory tools commonly used to determine the leachability and mobility of inorganic contaminants. Although a wide variety of leaching tests are available in the literature, most of them address the role of pH and complexation, and very few have been designed to address the question of the effect of changes in the redox potential (ORP) on contaminant release [1].

However, in the environment, many factors can significantly affect the oxidation–reduction status of contaminated soils such as periodic inundation, fluctuating groundwater levels, excess organic matter, increases in indigenous bacterial activity, revegetation, oxygen consumption by plant roots, or deterioration of soil physical properties [2–4]. The effect of reducing conditions can be substantial. Contaminant release can be affected by orders of magnitude either by direct reduction or by indirect effects such as precipitation of metal sulfides (e.g., CdS, CuS, FeS<sub>2</sub>, MnS, ZnS) [5] or dissolution of hydrous aluminum, iron and manganese oxides, releasing adsorbed or co-precipitated metals [6–14]. The development of a leaching test under reducing conditions is therefore critical for better evaluation of the risks to human health and

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ecological systems associated with a contaminated site and for improved management decisions. Assessment of the mobility of contaminants, such as arsenic, using experimentally induced and controlled reducing conditions will contribute to a better understanding of the competing geochemical and biological oxidation/reduction processes that affect contaminant fate, transformation, and transport in the subsurface environment.

In the laboratory, reducing conditions may be brought about by biological methods or the use of chemical reducing agents. Biological methods consist of batch incubation of the soil under flooded conditions to promote the specific activity of either indigenous or cultured anaerobic microorganisms [15–18]. These methods can take up to several weeks and are largely dependent upon the characteristics of the microorganisms and nutrients present in the soil. It is therefore difficult to control the processes that are occurring in the batch microcosm system, even more so to control the redox environment. In contrast, the use of chemical reducing agents can offer a simple and fast means by which to obtain different redox environments. However, most research on the chemical reduction of soils have been focused on using the techniques as remediation methods for heavy metal contaminated soils [19] and metal recovery in the metal processing industry [20–22]. Little research has been published on the use of chemical reducing agents as a tool to characterize the potential mobility of inorganic contaminants in soils under various pH and redox environments. Davranche et al. [7–9,23] reported the use of hydroxylamine hydrochloride and sodium ascorbate to study the effect of reductive dissolution on the mobility of heavy metals (i.e., Pb, Cd, Zn) from slag and synthesized and natural iron and manganese oxyhydroxides [10,11,13,14]. The use of sodium borohydride has been reported for the precipitation of cobalt by reduction [24], removal of copper from amino acid complexes [25], as well as for the extraction of copper, lead, and zinc from soil samples in combination with a chelant (EDTA or citric acid) [26].

The objectives of the research presented here were to evaluate (i) the ability of chemical reducing agents to produce different redox environments and (ii) the impact of reducing conditions on the mobility of arsenic from an industrial contaminated soil. A gold mining site, where arsenic-containing ores and tailings were exposed to weathering and erosion, was used for the study. Two chemical reducing agents were investigated: (i) sodium ascorbate and (ii) sodium borohydride. Sodium ascorbate was chosen because it is a mild reducing agent with a standard redox potential of +0.39 V (versus normal hydrogen electrode (NHE)) [10], which is lower than the potential (1 V) for the iron(III)/iron(II) redox couple, known for playing an important role in the redox chemistry of soils. Sodium borohydride was chosen because it is a very strong reducing agent with a redox potential of  $-1.24$  V (versus NHE) at pH 14, decreasing to  $-0.48$  V at pH 0 [24]. In addition, both reducing agents were expected to minimize the risks of precipitation or complexation (such as occurs with hydroxylamine hydrochloride or sodium sulfite).

Liquid–solid partitioning experiments were carried out in the presence of the reducing agents at different pH conditions. In addition to arsenic, iron concentration was also measured since amorphous iron(III) oxyhydroxides are known to play an important role in the mobility of arsenic [27–30].

## 2. Materials and methods

### 2.1. Soil sample collection and preparation

An arsenic-contaminated soil collected from a gold mining site in France, where mining activities and smelting processes of gold ores took place, was used for the study. A representative top-surface soil sample (depth: 5–35 cm) of about 50 kg was collected using a mechanical scoop. Prior to characterization and liquid–solid partitioning experiments, the soil was air-dried at room temperature ( $20 \pm 3$  °C) for one day, sieved at 2 mm through a stainless steel sieve (No. 10) to remove coarse debris and gravel, homogenized, and stored at 4 °C in the dark.

### 2.2. Soil sample characterization

The sand (50–2000  $\mu\text{m}$ ), silt (2–50  $\mu\text{m}$ ), and clay (<2  $\mu\text{m}$ ) fractions of the soil were determined using the NF X31-107 protocol [31]. Total content of trace elements and major soil constituents was determined by acid digestion [32] and subsequent analyses using inductively coupled plasma atomic emission spectrometry (ICP-AES; Jobin-Yvon Ultima 2<sup>®</sup>). The natural pH of the soil was measured on a soil slurry with a soil–water ratio of 1:10 (10 g of sample in 100 mL of deionized water) after a contact time of 48 h (SR003.1 protocol [33]) using an Accumet<sup>®</sup> combined glass electrode (Fisher Scientific). The redox potential of the soil was measured using an Accumet<sup>®</sup> metallic combination electrode (platinum/Ag/AgCl, +197 mV versus NHE, Fisher Scientific).

X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped for energy dispersive spectroscopy (EDS) analyses were used in conjunction with single [33–37] and sequential chemical extraction techniques [38].

XRD analyses were performed on three replicates of the less than 2 mm soil fraction grounded to powder (<50  $\mu\text{m}$ ) using a SIEMENS<sup>®</sup> D500 dual goniometer diffractometer with Cu K $\alpha$  radiation. The samples were scanned from 3° to 70°  $2\theta$  at a scan rate of 0.02°  $2\theta$ /s. The results obtained were processed using the DIFFRAC<sup>Plus</sup> EVA<sup>®</sup> software (BRUKER AXS<sup>®</sup>) and the International Centre for Diffraction Data database (ICDD<sup>®</sup>).

SEM-EDS analyses were performed on two replicates of the less than 2 mm soil fraction using a JEOL<sup>®</sup> 840A LGS scanning electron microscope equipped with a solid state Si(Li) (30 mm<sup>2</sup>) digital detector. Samples for SEM-EDS analyses were obtained by attaching the soil particles on an adhesive tape placed on a stub (sample holder of the SEM). No coating of the samples with a conductive material was

necessary prior to the analysis. An accelerating voltage of 20 kV was used for qualitative analyses. For each sample, secondary and backscattered electron images were collected to visualize the average chemistry and to locate the particles containing arsenic. X-ray mappings for Ca, As, Fe, S, and Si were then performed using a magnification of 200 $\times$  for identification of the relative distribution (complementary or correlating) of the different elements.

Single extraction techniques using deionized water, 0.01 mol L<sup>-1</sup> calcium chloride (CaCl<sub>2</sub>) solution, and 0.05 mol L<sup>-1</sup> ethylene diamine tetraacetic acid (EDTA) solution at pH 7 (end point pH obtained by addition of a pre-determined equivalent of potassium hydroxide prior to the beginning of the extraction), were performed to determine, respectively, the soluble, mobile, and available fractions in the soil [34,36]. These single extractions were carried out in triplicate using a liquid to solid (LS) ratio of 10 mL/g and a contact time of 48 h, except for the EDTA extraction for which an LS ratio of 100 mL/g was used. An end-point of pH 7 was used for the EDTA extraction in order to maximize the solubility of anions and oxy-anions by the use of neutral pH in parallel to the increase of cation solubility through chelation [35].

Additionally, a sequential chemical extraction procedure adapted from Matera et al. [29] was carried out in triplicate to determine the major, operationally defined, arsenic binding phases. The following seven fractions were examined:

- F1: arsenic soluble in MgCl<sub>2</sub> (magnesium chloride solution 1 mol L<sup>-1</sup> adjusted to pH 7.0);
- F2: arsenic bound to carbonates (sodium acetate solution 1 mol L<sup>-1</sup> adjusted to pH 4.5 with acetic acid);
- F3–Mn: arsenic bound to Mn-oxides (hydroxylammonium chloride 0.04 mol L<sup>-1</sup> in 25 (v/v) acetic acid at 96 °C);
- F3–Fe(a): arsenic bound to amorphous Fe oxides (0.2 mol L<sup>-1</sup> oxalate/oxalic acid);
- F3–Fe(c): arsenic bound to crystalline Fe oxides (0.2 mol L<sup>-1</sup> oxalate/oxalic acid with 0.1 mol L<sup>-1</sup> ascorbic acid);
- F4: arsenic bound to organic matter and sulfides (nitric acid 0.02 mol L<sup>-1</sup> and hydrogen peroxide 8.8 mol L<sup>-1</sup> at 85 °C followed by ammonium acetate solution 3.2 mol L<sup>-1</sup> in 20% (v/v) nitric acid);
- F5: residual fraction. This fraction was estimated from the total content obtained using acid digestion.

### 2.3. Liquid–solid partitioning experiments under oxidizing conditions

As a baseline, liquid–solid partitioning of arsenic and iron was determined under oxidizing conditions at varying pH. Eleven sub-samples of soil were contacted with solutions of varying equivalents of nitric acid or potassium hydroxide at an LS ratio of 10 mL/g to reach final pH ranging between 2 and 12 (SR002.1 protocol, solubility and release as a function of pH [33]). Triplicate assays were carried out. After 48 h, the

leachate pH and ORP of each subsample were measured prior to leachate filtration through a 0.45  $\mu$ m pore size polypropylene membrane and subsequently preserved with nitric acid until further analysis. The concentrations of arsenic and iron were then measured using flame atomic absorption spectrometry (FAAS, Varian Flame AA 640<sup>®</sup>).

### 2.4. Liquid–solid partitioning experiments under reducing conditions

Sodium ascorbate and sodium borohydride were used as the chemical reducing agents. Analytical grade chemicals were used and all solutions were prepared with doubly deionized water (Milli-Q system, Millipore). Two series of experiments were carried out for each reducing agent of concern. One series was carried out using varying concentrations of the reducing agent. In this series, the pH was controlled by the soil buffering capacity and the reducing agent used. The objective of this series was to determine the amount of reducing agent that was needed to reach different levels of ORP and to obtain a maximum effect on the solubilization of arsenic. The ranges of sodium ascorbate and sodium borohydride concentrations to be used were estimated based on an estimate of the soil oxidation capacity calculated using only the available fraction of iron (as determined using EDTA extraction) [2,3,7–9,39].

A second series of experiments was carried out using a constant concentration of the reducing agent and additions of sodium hydroxide or nitric acid (only in the case of sodium ascorbate) to control the pH at different values. The objective of this series was to determine the effect of pH on ORP and subsequently on the solubilization of arsenic and iron. The maximum concentration of reducing agent examined in the first series was used in this series of experiments. Although nitric acid is an oxidant and thereby directly affects ORP, it was preferred to other acids to minimize the risks of precipitation (e.g., such as occurs with sulfuric acid), complexation (e.g., with organic acids or hydrochloric acid), or analytical interferences [33].

For each series of experiments, 10 g sub-samples of soil were contacted with the solution of concern at an LS ratio of 10 mL/g. All assays were carried out in triplicate. A contact time of 48 h was used for the extractions with sodium borohydride. This contact time has been shown for aqueous solutions to provide adequate measurement of equilibrium [40] and is significantly greater than the contact time necessary for complete reaction with sodium borohydride [25]. A contact time of 10 days was used for the extractions with sodium ascorbate because of the slow reductive kinetics of this reagent [7,14]. High-density polyethylene leak-proof lid bottles were used for the extractions. The bottles were tumbled in an end-over-end fashion at a speed of 28  $\pm$  2 rpm at room temperature (20  $\pm$  2 °C). At the conclusion of the agitation, the bottles were removed from the rotary tumbler and transferred into a glove box that was continuously purged with nitrogen to avoid contact of the extracts with oxygen and prevent oxi-

dation and/or precipitation reactions. Final solution pH and ORP were then measured and the liquid and solid were separated by pressure filtration with nitrogen through a 0.45  $\mu\text{m}$  pore size polypropylene Gelman Sciences® membrane. The ORP was measured using an Accumet® metallic combination electrode (platinum/Ag/AgCl, +197 mV versus NHE). Filtered liquid solutions obtained from the extractions were then refrigerated at 4 °C before subsequent chemical analysis. Arsenic and iron concentrations were then measured using FAAS.

### 3. Results and discussion

#### 3.1. Soil sample characterization

The soil consisted of 63 wt% sand, 24.6 wt% silt, and 12.4 wt% clay and contained ca. 3 wt% arsenic, ca. 9 wt% iron, and ca. 1.9 wt% total organic compounds [34]. Total content of trace and major elements of the soil are summarized in Table 1. The soil presented a natural pH of 6.5 and an ORP of +400 mV (versus NHE).

XRD analyses indicated the presence of traces of hematite ( $\text{Fe}_2\text{O}_3$ ) and jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), which are the common pyrite weathering products with which arsenic can be typically associated [41]. No pyrite ( $\text{FeS}_2$ ) or crystallized arsenic mineral phases such as arsenopyrite ( $\text{FeAsS}$ ), however, were detected in the soil. The main crystallized mineral phases observed were quartz, gypsum, feldspars, muscovite, calcite, and dolomite. The absence of residual mixed sulfide phases in the soil was attributed to the weathering and oxidation of pyritic minerals during the post-mining period.

SEM–EDS results (Fig. 1) showed a close similarity between the arsenic and iron cartography. Arsenic and iron, although at high content in the soil (ca. 2.7 and 8.9%, re-

Table 1

Total content of major and trace elements as determined by acid digestion—arsenic contaminated soil

Si (%)	20.3
Fe (%)	8.9
Al (%)	4.3
Ca (%)	3.7
S (%)	2.1
K (%)	1.9
Mg (%)	0.6
Na (%)	0.1
As ( $\text{mg kg}^{-1}$ )	27700
Cu ( $\text{mg kg}^{-1}$ )	1700
Pb ( $\text{mg kg}^{-1}$ )	800
Mn ( $\text{mg kg}^{-1}$ )	400
Zn ( $\text{mg kg}^{-1}$ )	400

spectively), were not located in any of the main crystallized phases. Arsenic seemed to have been sorbed with the iron on the soil particles. The presence of amorphous arsenic-bearing phases, such as iron oxyhydroxides, was therefore suspected [18,34] and thought to be the major process of arsenic trapping in the soil. This assumption, which is consistent with results found in the literature [28,29,42–44] was also evidenced by complementary mineralogical analyses conducted on the soil by the French Geological Survey (BRGM, Orléans) [41] and the results obtained from the Matera et al. [29] sequential extraction procedure.

Results from the single and sequential extractions performed on the soil are summarized in Table 2. Very low soluble (ca. 0.016%) and mobile (ca. 0.013%) fractions of arsenic were obtained from the single extraction procedures using deionized water and calcium chloride, respectively, as the extractant. A significant available fraction of arsenic was, however, observed from the single extraction using EDTA (ca. 40% of total arsenic content was extracted). In contrast, results from the sequential extraction procedure indicated that

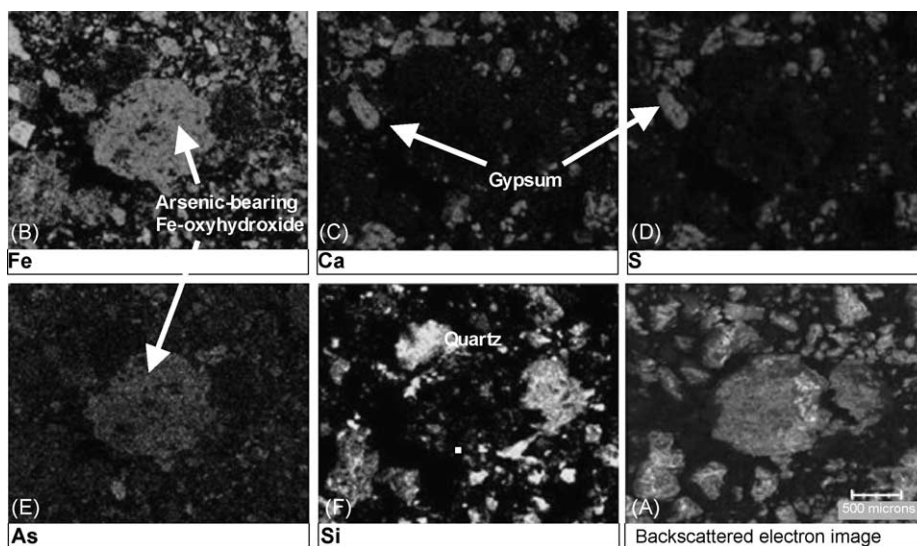


Fig. 1. SEM–EDX mapping of the less than 2 mm fraction of the arsenic contaminated soil (200 $\times$ ). (A) SEM image and the corresponding EDX mapping of (B) iron, (C) calcium, (D) sulfur, (E) arsenic, and (F) silicon.

Table 2

Results from the single and sequential chemical extractions performed on the less than 2 mm arsenic contaminated soil fraction (concentration in  $\text{mg kg}^{-1}$ )

	As	Fe
Soluble fraction (deionized water)	3.8	0.2
Mobile fraction ( $\text{CaCl}_2$ )	3.2	0.1
Available fraction (EDTA)	11800	22500
Sequential extractions		
F1: arsenic soluble in $\text{MgCl}_2$	2.7	2.0
F2: arsenic bound to carbonates	43	30
F3–Mn: arsenic bound to Mn-oxides	1305	13523
F3–Fe(a): arsenic bound to amorphous Fe oxides	18384	31637
F3–Fe(c): arsenic bound to crystalline Fe oxides	444	9666
F4: arsenic bound to organic matter and sulfides	6.7	330
F5: residual fraction (not extracted)	7515	33613

arsenic was fairly mobile. About 72% of the total content in arsenic was extracted within the first four extracts with ca. 67% extracted as the fraction bound to amorphous Fe oxides. Only 27% of the total content in arsenic was in the residual fraction (i.e., silicates, sulfides, or resistant organic matter). These results indicated that most of the arsenic was bound onto As-bearing-Fe-oxyhydroxides, which is consistent with results from the XRD and SEM study. Additionally, concurring with what is generally observed [29], iron was essentially mobilized in the fractions F3–Fe(a), F3–Fe(c), and F5 (residual). A significant iron extraction percentage (ca. 15%) could also be observed in the F3–Mn fraction.

### 3.2. Effect of sodium ascorbate addition

Four different sodium ascorbate concentrations that provided different levels of ORP were examined: 0.0075, 0.01, 0.025, and  $0.046 \text{ mol L}^{-1}$ .

The effect of sodium ascorbate addition on pH and ORP is shown in Fig. 2A and B, respectively. Sodium ascorbate addition slightly modified the final pH for the concentration range studied. A small decrease of ca. 0.4 pH unit was observed. In contrast, a significant decrease in ORP was observed. The largest change in ORP was noted between the concentrations of  $0.01 \text{ mol L}^{-1}$  (ca. +345 mV versus NHE) and  $0.025 \text{ mol L}^{-1}$  (ca. +5 mV versus NHE).

The effect of sodium ascorbate addition on the liquid–solid partitioning of arsenic and iron is shown in Fig. 3A and B, respectively. The liquid–solid partitioning as a function of pH obtained under oxidizing conditions is also shown as a baseline. The solubilization of arsenic and iron was significantly increased by the addition of sodium ascorbate for all concentrations examined (as much as three orders of magnitude and four orders of magnitude, respectively, for the addition of  $0.046 \text{ mol L}^{-1}$  of sodium ascorbate).

For low additions of sodium ascorbate (i.e.,  $0.0075$  and  $0.01 \text{ mol L}^{-1}$ ) that yielded no significant change in the ORP, the increase in arsenic and iron solubilization seemed to be indicative of a reductive dissolution of iron oxyhydroxides [10,14] with reduction of surface iron(III) sites. The release of iron was accompanied by a simultaneous release of sorbed arsenate. For additions of sodium ascorbate that yielded a decrease in the ORP to values close to or below 0 mV versus NHE (i.e.,  $0.025 \text{ mol L}^{-1}$  of sodium ascorbate), the increase in arsenic solubilization was thought to be attributed to changes in arsenic speciation with the conversion of As(V) to the more soluble As(III) in the solid arsenic mineral phases, in addition to the reduction and dissolution of “ferric arsenates,” which is generally considered to be the primary controlling mechanism under moderately reduced soil conditions [28,43]. This assumption was supported by the pH–Eh diagram of the system As–O–H at  $25^\circ\text{C}$  and 1 bar [45], which indicated a transition from As(V) to As(III) near the pH and Eh of concern (pH of ca. 7 and Eh close to 0 mV versus NHE). In addition, recent experiments with synthetic iron and aluminum oxides on bio-reduction demonstrated the desorption of arsenic following reduction of As(V) to As(III) [46] at the onset of strongly reducing conditions near-neutral pH providing evidence that the dissolution of the oxides is not necessary for the release of arsenic. Further addition of sodium ascorbate did not have further effect on either the ORP or the solubilization of arsenic and iron. This result suggested that the iron oxyhydroxides became saturated with respect to the solution (i.e., re-adsorption of ferrous iron onto the surface of iron(III) oxyhydroxides, thus limiting the further dissolution reaction), resulting in a reductive dissolution rate independent of sodium ascorbate concentration [12,47].

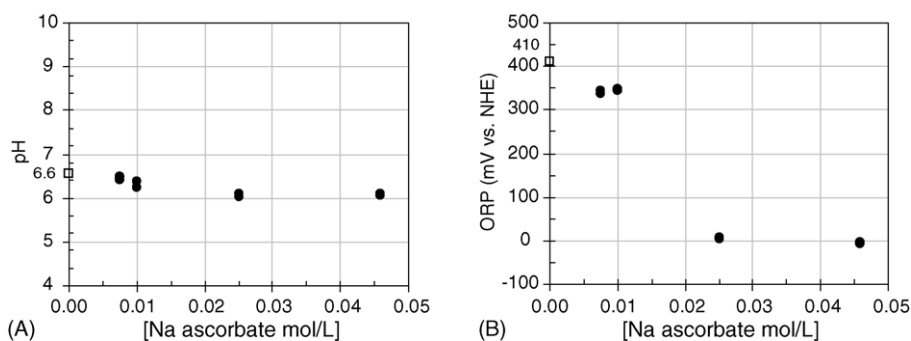


Fig. 2. Effect of sodium ascorbate addition (●) on (A) pH and (B) ORP. pH and ORP at the natural conditions of the soil are also provided (□) (LS ratio: 10 mL/g; contact time: 10 days).

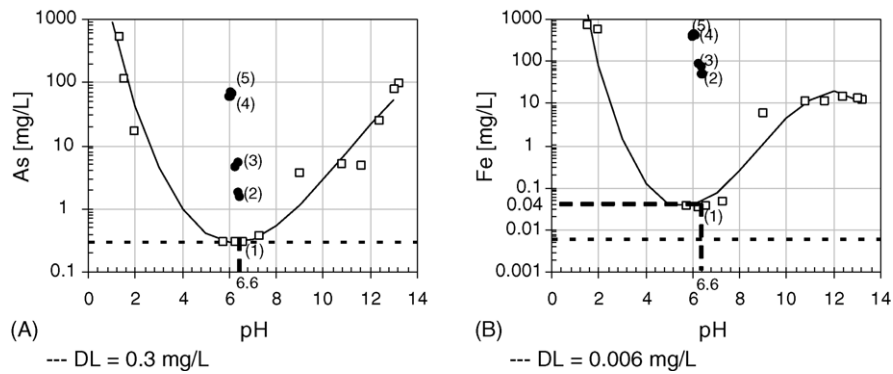


Fig. 3. Effect of sodium ascorbate addition (●) on the liquid–solid partitioning of (A) arsenic and (B) iron. Baseline liquid–solid partitioning as a function of pH obtained under oxidizing conditions is shown for comparison (□) (DL: detection limit). (1) Baseline, ORP=410 mV vs. NHE; (2) 0.0075 mol L<sup>-1</sup>, ORP=340 vs. NHE; (3) 0.01 mol L<sup>-1</sup>, ORP=345 mV vs. NHE; (4) 0.025 mol L<sup>-1</sup>, ORP=5 mV vs. NHE; (5) 0.046 mol L<sup>-1</sup>, ORP=-7 mV vs. NHE.

### 3.3. Effect of varying pH for constant concentrations of sodium ascorbate

The liquid–solid partitioning of arsenic and iron at varying pH in the presence of a constant concentration of sodium ascorbate (i.e., 0.025 mol L<sup>-1</sup> or 0.046 mol L<sup>-1</sup>) is shown in Fig. 4A and B, respectively. The liquid–solid partitioning as a function of pH obtained under oxidizing conditions is also shown as a baseline. The two concentrations of sodium ascorbate used corresponded to the concentrations that provided the lowest ORP. pH values ranging from 5.8 to 10.3 were examined. ORP varied from ca. +10 mV versus NHE (pH ca. 5.8) to -160 mV versus NHE (pH ca. 10.3) for both sodium ascorbate concentrations. Lower ORP could not be obtained for the most acidic pH since nitric acid, which is a strong oxidizing reagent, was used to lower the pH.

The addition of sodium ascorbate enhanced both arsenic and iron solubilization over the pH range tested. However, no significant difference in ORP and arsenic and iron solubilization was seen between the two concentrations of sodium ascorbate. The largest increase in solubilization compared to the baseline was observed for the lowest pH tested (as much as three orders of magnitude for arsenic and four orders of

magnitude for iron at pH ca. 6). This result was consistent with previous studies performed by Stumm et al. [14] and Deng [10] that indicated that the reductive dissolution of iron oxyhydroxides with ascorbate increases with decreasing pH and could be interpreted by the pH dependence of the extent of ascorbate adsorption onto the surface of iron oxyhydroxides.

### 3.4. Effect of sodium borohydride addition

Fig. 5A and B show the effect of sodium borohydride addition on the pH and ORP, respectively. Five different sodium borohydride concentrations were examined: 0.0075, 0.01, 0.025, 0.046, and 0.075 mol L<sup>-1</sup>. In contrast with sodium ascorbate (Fig. 2), the addition of sodium borohydride had a stronger effect on pH, with final pH values ranging from 7.2 to 9. Additionally, a broader ORP range was obtained, yielding “highly” reduced soil conditions (from ca. +140 to -500 mV versus NHE), compared to moderately reduced soil conditions obtained with the addition of sodium ascorbate (from ca. +345 to -7 mV versus NHE). A significant decrease in the ORP to a value of ca. -440 mV versus NHE was observed for the addition of sodium borohydride at a concen-

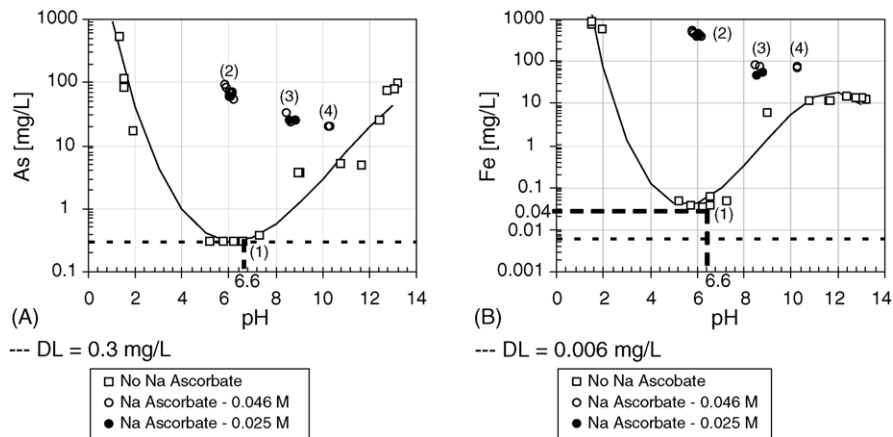


Fig. 4. Effect of varying pH in the presence of sodium ascorbate (0.025 mol L<sup>-1</sup> (●) and 0.046 mol L<sup>-1</sup> (○)) on the liquid–solid partitioning of (A) arsenic and (B) iron. (1) Baseline, ORP=410 mV vs. NHE; (2) ORP=10 mV vs. NHE; (3) ORP=-35 mV vs. NHE; (4) ORP=-160 mV vs. NHE.

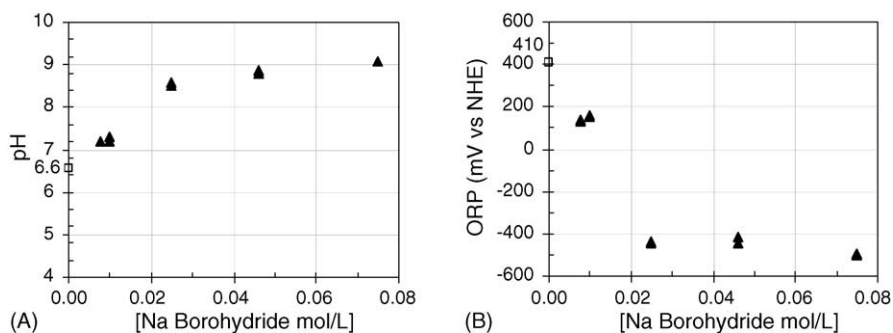


Fig. 5. Effect of sodium borohydride addition (▲) on (A) pH and (B) ORP. pH and ORP at the natural conditions of the soil are also provided (□) (LS ratio: 10 mL/g; contact time: 48 h).

tration of  $0.025 \text{ mol L}^{-1}$ . Addition of sodium borohydride at higher concentrations did not significantly change the ORP or the pH. This result was similar to that obtained with sodium ascorbate.

Addition of sodium borohydride enhanced the solubilization of arsenic (Fig. 6A) over the pH range tested. For a given pH value, arsenic solubilization obtained in the presence of sodium borohydride was increased by as much as one order of magnitude compared to the baseline solubilization with no sodium borohydride. In contrast to arsenic solubilization, iron solubilization was not significantly affected by the ORP conditions provided by sodium borohydride over the pH range tested (Fig. 6B). For a given pH, although lower ORP were reached in the presence of sodium borohydride compared to sodium ascorbate, the addition of sodium borohydride provided lower solubilization of arsenic and iron compared to that obtained with the addition of sodium ascorbate. The concentration of arsenic and iron in the ORP range of 5–340 mV in sodium ascorbate experiments (Fig. 3, points 2, 4) was higher than that in the middle of this range (i.e., ORP of ca. +150 mV) in the case of sodium borohydride (Fig. 6, points 2, 3), while the pH was similar (6.6 and 7.1, respectively). Thus, at similar ORP–pH conditions the results of extraction for arsenic and iron were different for the two reagents used. This result may indicate the potential effect of the nature of the reagents, resulting in different reaction mecha-

nisms for iron and arsenic release. In addition to the nature of the reagents, the low solubilization of iron observed in the sodium borohydride experiments compared to the sodium ascorbate experiments at a given pH could be due to iron precipitation in the anoxic soil system as sulfide. The studied mining soil contained gypsum, whose leaching resulted in ca.  $1.5 \text{ g L}^{-1}$  sulfate in the soil solution. Under the chemical conditions provided by sodium borohydride (i.e., alkaline and “highly” reduced soil conditions) sulfate reduction might have occurred, promoting iron immobilization into sulfide solids. Using thermodynamic calculations, Sadiq [43] showed that iron concentrations in highly reduced soils are mainly controlled by the precipitation and dissolution equilibrium of pyrite [ $\text{FeS}_2$ ]. In turn, arsenic solubilization in the sodium borohydride experiments could have been affected by arsenic co-precipitation with or sorbed onto iron sulfide and/or formation of arsenic sulfide [48,49].

### 3.5. Effect of pH for a constant concentration of sodium borohydride

Arsenic and iron liquid–solid partitioning as a function of pH in the presence of a constant concentration of sodium borohydride (i.e.,  $0.046 \text{ mol L}^{-1}$ ) is shown in Fig. 7A and B, respectively. The sodium borohydride concentration used here corresponded to the lowest concentration of sodium

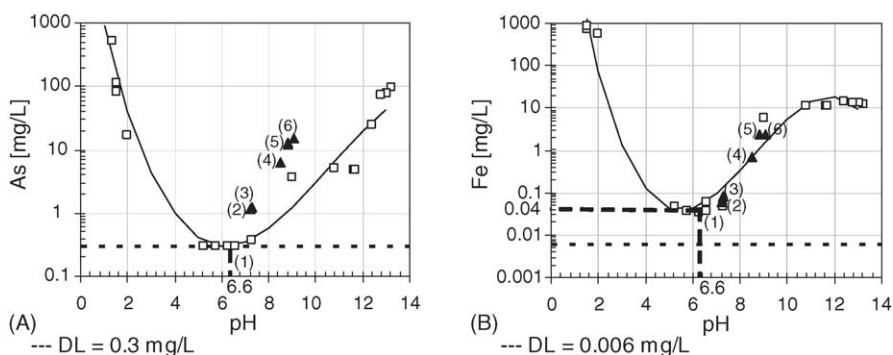


Fig. 6. Effect of sodium borohydride concentration (▲) on the liquid–solid partitioning of (A) arsenic and (B) iron. Baseline liquid–solid partitioning as a function of pH obtained under oxidizing conditions is shown for comparison (□). (1) Baseline, ORP = 410 mV vs. NHE; (2)  $0.0075 \text{ mol L}^{-1}$ , ORP = 140 mV vs. NHE; (3)  $0.01 \text{ mol L}^{-1}$ , ORP = 150 mV vs. NHE; (4)  $0.025 \text{ mol L}^{-1}$ , ORP = -440 mV vs. NHE; (5)  $0.046 \text{ mol L}^{-1}$ , ORP = -445 mV vs. NHE; (6)  $0.075 \text{ mol L}^{-1}$ , ORP = -500 mV vs. NHE.

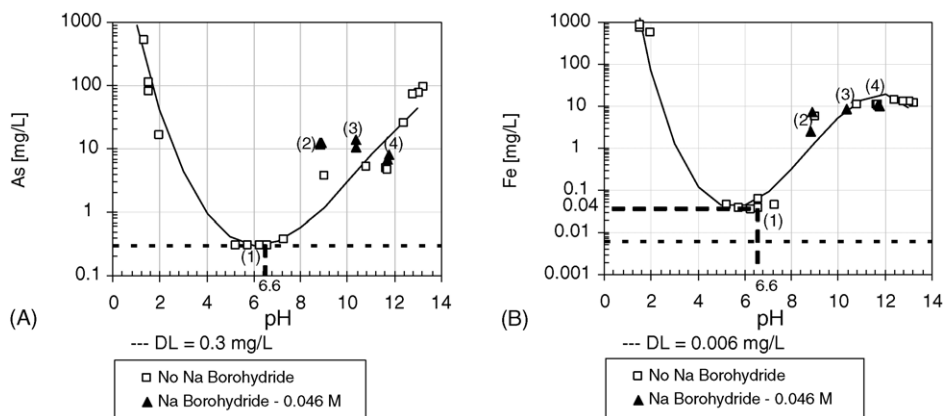


Fig. 7. Effect of varying pH in the presence of sodium ascorbate ( $0.046 \text{ mol L}^{-1}$ ) ( $\blacktriangle$ ) on the liquid–solid partitioning of (A) arsenic and (B) iron. (1) Baseline, ORP = 410 mV vs. NHE; (2) ORP =  $-430$  mV vs. NHE; (3) ORP =  $-650$  mV vs. NHE; (4) ORP =  $-780$  mV vs. NHE.

borohydride that provided the maximum change in pH and ORP. pH values ranging from ca. 8.8 to 11.8 were examined. A range of ORP between ca.  $-800$  mV versus NHE (obtained at a pH value of 11.8) and ca.  $-500$  mV versus NHE (at a pH of 8.8) was measured. This ORP range was significantly lower than that obtained with sodium ascorbate for similar pH (i.e.,  $-160$  mV versus NHE for pH ca. 10.3).

The increase in arsenic solubilization at a given pH (Fig. 7A) was again less significant than that observed with sodium ascorbate (Fig. 4A), although lower ORP conditions were obtained. For pH values between ca. 10 and 12, no significant effect on arsenic solubilization was observed. Iron solubilization (Fig. 7B) was not significantly affected by ORP conditions over the pH range examined (i.e., ca. 9–12). No significant differences were observed between iron solubilization obtained in the presence of sodium borohydride and the baseline iron solubilization, even though significant changes in ORP conditions were observed for a given pH value. These results differed from that obtained with sodium ascorbate for which a significant increase in arsenic and iron solubilization was observed over the entire pH range tested (Fig. 4A and B). These results seemed to confirm that the geological background of the soil and the alkaline and extreme anoxic soil conditions obtained using sodium borohydride might have led to iron precipitation as sulfide and arsenic coprecipitation with this mineral and/or formation of arsenic sulfide [48,49].

#### 4. Conclusions

A method for estimating the release of contaminants from contaminated sites under reducing conditions has been proposed. The ability of two chemical reducing agents, sodium ascorbate and sodium borohydride, to produce different redox environments in a mining soil was investigated.

Sodium borohydride provided greater reducing conditions (ranging from  $-500$  to  $+140$  mV versus NHE) than sodium ascorbate (ranging from  $-7$  to  $+345$  mV versus NHE). In-

dependent of the reducing agent used, reducing conditions significantly enhanced the solubilization of arsenic compared to that obtained under oxidizing conditions (by as much as three orders of magnitude for sodium ascorbate and one order of magnitude for sodium borohydride). The addition of sodium ascorbate significantly increased the solubilization of arsenic and iron for all concentrations examined and pH tested, although the reducing conditions obtained were mild. This effect was most pronounced under slightly acidic conditions (as much as three orders of magnitude and four orders of magnitude, respectively, for the addition of  $0.046 \text{ mol L}^{-1}$  of sodium ascorbate at a pH of ca. 6). While the mechanisms remain uncertain, it was thought that both reductive dissolution of “ferric arsenates” and changes in the arsenic speciation in the solid phase of the arsenic minerals (reductive desorption) may have played a role in the release of arsenic and iron. In contrast to sodium ascorbate, the alkaline and highly reduced soil conditions obtained with sodium borohydride led to a lower effect on arsenic solubilization (as much as one order of magnitude for pH between ca. 7 and 10 and no effect for pH values between ca. 10 and 12) and no effect on iron solubilization for all concentrations examined and pH tested. At similar ORP–pH conditions the results of extraction for arsenic and iron were different for the two reagents used, suggesting the potential effect of the nature of the reagents. In addition to the nature of the reagents, the low solubilization of iron observed in the sodium borohydride experiments compared to the sodium ascorbate experiments could be due to iron precipitation in the anoxic soil system as sulfide.

This research confirmed the importance of the oxidation–reduction status of a contaminated soil and the need for a simple and fast laboratory method by which to obtain different redox environments. Experimentally induced and controlled reducing conditions can allow for intrinsic characterization of the potential mobility of contaminants in a contaminated soil and for better understanding of the geochemical oxidation/reduction processes that affect contaminant fate, transformation, and transport in the subsurface environment. Further improvement in the testing of the method proposed



here could result in establishing a protocol for solubility and release of contaminants under reducing conditions, which is critical for better evaluation of the risks associated with a contaminated site.

## Acknowledgements

The research presented in this paper was supported by the Consortium for Risk Evaluation with Stakeholder Participation (CRESP, USA), the Association RE.CO.R.D. (Waste Research Cooperative Network, France), and the Région Rhône-Alpes. The authors are grateful to Professor Lyliane Faure for many helpful discussions and thoughtful review comments.

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