



## Environmental impact of As(V)–Fe oxyhydroxide reductive dissolution: An experimental insight

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### ABSTRACT

Polymer slides covered by synthetic As-spiked ferrihydrite (As-Fh) or As-spiked lepidocrocite (As-Lp) were inserted into an organic-rich wetland soil in non conventional columns system under anaerobic conditions. Slides were recovered after different periods of time to evaluate (i) the impact of (bio)reduction on both Fe-oxide dissolution and secondary mineral precipitation and, (ii) the subsequent effects on As mobility. The calculated Fe dissolution rates for As-Fh and As-Lp were  $2.02 \cdot 10^{-9}$  and  $1.92 \cdot 10^{-9}$  mol Fe  $m^{-2} s^{-1}$ , respectively, and were higher than what has been commonly reported in laboratory studies. Important bacterial colonization and occurrence of biofilm suggest the presence of biologically mediated processes. The newly formed minerals were mostly composed of Fe-sulphides. Fe(II) complexation by organic molecules in solution likely prevented formation of secondary Fe(II, III)-rich minerals. The relative proportion of As(III) increased with time on the As-Fh slides, and was combined with a decrease of the Fe/As ratio, suggesting a partial adsorption of As(III) onto minerals. By contrast, for lepidocrocite, the Fe/As ratio increased, suggesting that As(III) was less re-adsorbed due the lower available site number and the deletion of As adsorption sites on the reduced lepidocrocite surface. Reduction and subsequent As sequestration appeared to result from a coupled biotic–abiotic reaction pathway in which Fe or As reducing-bacteria allowed the reduction of As(V) to As(III).

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### 1. Introduction

Iron (III) oxyhydroxides are of particular environmental relevance because they often occur as fine grained particles and exhibit high reactive surfaces (Tipping et al., 1981; Scheidegger et al., 1993; Kaplan et al., 1997; Fox and Doner, 2002). The Fe(II)/Fe(III) redox couple is an important electron-transfer mediator for many biological and chemical species. As a consequence, the stability of Fe(III) oxyhydroxides in soils exerts a major control on mobility of both organic (Amonette et al., 2000; Williams and Scherer, 2004; Tobler et al., 2007) and inorganic pollutants such as arsenic (Ahmann et al., 1997; Davranche and Bollinger, 2000a,b; Zobrist et al., 2000; Zachara et al., 2001; Fox and Doner, 2002; Davranche et al., 2003; Chatain et al., 2005).

The importance of microorganisms in the biogeochemical cycling of Fe is well-recognized (Lovley and Phillips, 1986; Lovley, 1991; Lovley et al., 1991; Wahid and Kamalam, 1993; Roden and Zachara, 1996). Iron-reducing bacteria – which are ubiquitous in waterlogged soils and aquifers – couple the oxidation of organic matter with the reduction of various Fe(III) oxyhydroxides for their metabolism. A direct consequence of Fe(III) reduction is the associated trace metal release into soil solution (e.g. Schwertmann and Taylor, 1989; Lovley and Coates, 1997; Davranche and Bollinger, 2000a; Quantin et al., 2001; Zachara et al., 2001; Van Geen et al., 2004; Burnol et al., 2007; Jönsson and Sherman, 2008). However, recent studies have shown that arsenic can efficiently adsorb onto mineral resulting from Fe-oxides bioreduction (Kocar et al., 2006; Wang et al., 2008b), from Fe(II) promoted reduction of Fe-oxides (Pedersen et al., 2006), or resulting from the co-precipitation of Fe(II) and Fe(III) (Wang et al., 2008a).

Arsenic is strongly adsorbed onto Fe-oxides (Manning et al., 1998; Raven et al., 1998; Dixit and Hering, 2003), which are probably the most important carriers of As in aquifers and soils (Morin et al., 2002;

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Cancès et al., 2005; Morin and Calas, 2006; Cancès et al., 2008). Arsenic occurs at concentrations exceeding drinkable levels in major aquifers in several parts of the world, especially in South Asia (Smedley and Kinniburgh, 2002; Islam et al., 2004; Van Geen et al., 2008). High As concentrations in subsurface waters result often from reductive dissolution of hydrous Fe-oxides and subsequent release of associated As (Nickson et al., 2000; Bose and Sharma, 2002; Van Geen et al., 2004).

Several laboratory studies reported that As(V) is mainly adsorbed onto Fe-oxide surfaces and is not incorporated into the crystal lattice, even during coprecipitation (Waychunas et al., 1993; Raven et al., 1998; Randall et al., 2001; Sherman and Randall, 2003; Pedersen et al., 2006). These studies provided also evidence that As solubilisation rates and behaviour are dependent on both the mineralogical type of Fe-oxyhydroxide and its degree of crystallization. Pedersen et al. (2006) demonstrated through studies involving ferrihydrite and goethite submitted to chemical reduction that As(V) was not released before the surface site number became too small to adsorb all the available As. In the case of lepidocrocite, it has been reported that arsenic is mainly adsorbed by a double-corner sharing complex developed on the edge of the layers (setting Cmc21) where oxygen are singly coordinated on the 100 crystal plane (Randall et al., 2001; Cornell and Schwertmann, 2003; Sherman and Randall, 2003; Pedersen et al., 2006). Furthermore, Larsen and Postma, (2001) provided evidence by MET analysis that chemical reductive dissolution preferentially destroyed this elongated and strongly exposed (100) plane. Recent studies showed that the transformation of Fe-oxides catalysed by Fe(II) under reductive conditions induces the production of more reactive solid phases such as magnetite, green-rusts, ferrous iron carbonate and amakinite which efficiently bind As(V) and As(III) (Kocar et al., 2006; Wang et al., 2008a; Ona-Nguema et al., in press; Wang et al., 2008b). Formation of Fe(II,III) minerals may thus be important trapping mechanism for arsenic, notably in reducing environments where Fe concentration is sufficiently high to ensure over-saturation with respect to these minerals. Furthermore in organic rich-soil, organic compounds, including bacterial surfaces (Châtellier and Fortin, 2004), may complex Fe(II) and thus inhibit the formation of secondary Fe(II,III) minerals. For instance, Pedersen et al. (2006) showed when using ascorbic acid as reducer instead of Fe(II) that arsenic was mobilized upon reduction of As(V)-ferrihydrite and As(V)-lepidocrocite. Moreover, arsenic may compete with a number of other anions as carbonates (Burnol et al., 2007; Stachowicz et al., 2007) and organic anions for surface sites on Fe-oxyhydroxides (e.g. Bauer and Blodau, 2006; Slowey et al., 2007) or secondary Fe(II,III) minerals.

In the natural environment, the mineral soil matrix could also strongly influence the mechanism of the reductive dissolution and therefore the nature of the secondary mineral (for example, due to Fe(II) adsorption, the solubilisation of As). Until recently, it was extremely hard to gain an understanding of the involved processes in the natural environment. Studying mineralogical transformations of solids in situ in soils still remains a challenge. However, Fakh et al. (2008) developed a method inspired from Birkefeld et al. (2005) to monitor the transformation of Fe-oxides directly within soils and to quantify their reductive dissolution. Iron-oxides are precipitated onto acrylic slides which can be directly inserted into the soil. Iron-oxides particles can thereby interact with the surrounding soil components (minerals, organic matter and soil solution). Moreover the designed supports can be easily recovered from the soil matrix and the solid phases can subsequently be analyzed.

In the present study, we investigated the reductive dissolution of As-spiked ferrihydrite (As-Fh) and As-spiked lepidocrocite (As-Lp). A non conventional anaerobic column experiment was performed to stimulate reduction in a natural soil sample. Slides covered with either As-Fh or As-Lp were inserted directly into the soil (Fakh et al., 2008). The slides were recovered through time and then analyzed by XRF, SEM-EDS and X-ray Absorption Near Edge Structure (XANES). The

aims of this study were (i) to determine the dissolution rates of two different types of Fe-oxides in a waterlogged organic-rich soil, (ii) to study the mineralogical evolution of the Fe-oxides and, (iii) to evaluate the impact of these evolutions on As release.

## 2. Materials and methods

All chemicals used were of analytical grade. The solutions were prepared with doubly de-ionised water (Milli-Q system, Millipore). The containers used were (i) soaked in 10% ultrapure HNO<sub>3</sub> for 48 h at 60 °C to remove all possible contaminants sources, (ii) then rinsed with Milli-Q water for 24 h at 60 °C, and (iii) finally dried at 30 °C.

### 2.1. Iron oxide-covered slides

A technique based on slides coated by Fe-oxyhydroxides (Birkefeld et al., 2005; Fakh et al., 2008) was used. The tool consists of small (2×2×0.2 cm) striated polymer plates covered by synthetic As(V)-ferrihydrite (As-Fh), or As(V)-lepidocrocite (As-Lp). The detailed methodology for the production of the slides, their characterization and the method validation are further detailed in Fakh et al. (2008). Both Fe-oxides, weakly crystallized 2-line ferrihydrite and mildly crystallized lepidocrocite, were synthesized in the presence of As(V) (around 1% in weight) according to the Schwertmann and Cornell protocol (2000). The final ratio As/Fe is 0.005 in mol/mol.

### 2.2. Soil sampling

The soil was sampled from an organic-rich soil horizon in a wetland located in the Kervidy-Naizin catchment (North western, France). The soils developed into a loamy material derived from bedrock (Proterozoic schists) (Dabard et al., 1996) weathering and eolian Quaternary deposits, exhibit facies variations, which are locally dominated by silt, clay or sandstone materials (Pellerin and Van Vliet-Lanoë, 1994). The mineralogical composition of schist was determined from drill cutting analysis and include (in decreasing relative proportion): quartz, muscovite, chlorite, K-feldspar and plagioclase (Pauwels et al., 1998). The soil horizons comprise a large number of secondary mineral phases including illite, smectite, kaolinite, various Fe-oxides, and Fe-oxyhydroxides (hematite, goethite,...) and Mn-oxides (Curmi et al., 1998; Pauwels et al., 1998). This catchment is particularly well adapted to study Fe reductive dissolution because redox cycles involving Fe were highlighted in these soils (Dia et al., 2000; Olivé-Lauquet et al., 2001). The collected soil sample was dried at 30 °C during 72 h, and then sieved to 2 mm. The total concentrations of major and trace elements were analyzed by ICP-MS (trace elements) and ICP-AES (minor elements) following a lithium metaborate fusion. The loss of ignition was measured as an indicator of the carbon content. The major element concentrations in the soil are given in Table 1. The soil contained 1.03 wt.% of Fe, 15.1 wt.% of organic matter and 7.48 µg g<sup>-1</sup> of As.

### 2.3. Experimental set-up

Columns suited for anaerobic conditions were designed to investigate the influence of soil reduction on the Fe-oxide dissolution (Fig. 1). This technique was developed to allow the insertion of slides into a structured soil sample and to avoid the mechanical abrasion of oxides from slides that would occur in an equilibrium batch system under stirring. The anaerobic column can be described as follows: it consists of two reservoirs connected together by a flexible tygon tube of 0.2 mm internal diameter. The solution was continuously carried through the soil column using a peristaltic pump (Ismatec Ecoline) placed just before the entry into the upper reservoir (so-called 'soil' reservoir) (Fig. 1). The solution circulated in closed system and the percolating solution reached a steady state. The columns were thus

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