



# Evidence of organic matter control on As oxidation by iron oxides in riparian wetlands

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## ABSTRACT

Soils in riparian wetlands are periodically flooded, resulting in the establishment of reducing conditions and the solubilization of As, subsequently to the reductive dissolution of Fe(III)-oxyhydroxides. When the water level decreases, the wetlands are reoxidized. However, although the behavior of As under the reducing period is well documented, there is a lack of information regarding its behavior during the oxidizing period.

In this study, we investigated As speciation in oxidation products from an initially reduced wetland soil solution recovered from the Naizin-Kervidy riparian wetland (France). The oxidation products were studied using NanoSIMS analysis and synchrotron X-ray techniques. These products were enriched in organic carbon, Fe and As compared with the soil and soil solution. The NanoSIMS analysis showed a colocalization of As and Fe but also revealed the presence of As hotspots where As was either associated with Fe or organic matter (OM). X-ray absorption spectroscopy (XAS) showed that As was sorbed to Fe(III)-oxyhydroxides. The linear combination fitting (LCF) of the As K-edge XANES revealed that As was not totally oxidized (i.e. between 65 and 100% of As(V)). Shell-by-shell fits of the As K-edge EXAFS showed that As formed binuclear edge-sharing <sup>2</sup>E ( $R_{As-Fe} = 2.74\text{--}2.95\text{ Å}$ ) and corner-sharing <sup>2</sup>C ( $R_{As-Fe} = 3.28\text{--}3.43\text{ Å}$ ) complexes with Fe.

In addition to study of natural samples, oxidized reference samples were analyzed and demonstrated the role of OM on As speciation. The persistence of As(III) was explained by OM control on the As carrying phase during the oxidation, via the formation of nano-lepidocrocite and small Fe-clusters bound to OM. The small size of the Fe phase led to an increased capacity for As adsorption and an increase in <sup>2</sup>E sites compared to <sup>2</sup>C active sites for As(III) oxidation.

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## 1. Introduction

Among wetlands, riparian wetlands are of major importance for contaminant (organics, metals, metalloids, etc.) mobility in the environment. In wetlands during high water levels, reducing conditions are established and favor the reductive dissolution of Fe(III)-oxyhydroxides. The biogeochemical cycle of arsenic is strongly dependent on Fe(III)-oxyhydroxides. Their reductive dissolution leads to the release of As(V) along with Fe(II) and organic matter (OM) in the solution (Davranche et al., 2011; Dia et al., 2015; Grybos et al., 2007, 2009; Olivié-Lauquet et al., 2001). Following its solubilization, As(V) is reduced to As(III), generally by autochthonous bacteria (through detoxification or metabolism processes; Dia et al., 2015). Recent studies have shown that, under such reducing conditions, As(III) might be bound to

colloidal or particulate OM via thiol (–SH) groups and/or form ternary complexes, OM-Fe(II)-As, with Fe(II) as cationic bridges (Langner et al., 2012; Mikutta and Kretzschmar, 2011; Catrouillet et al., 2014). In the Mekong flood plain (Cambodia), several studies have demonstrated that subsequently to its release and reduction, As(III) is mobile and contaminates the underlying groundwater; these wetlands are thus considered to be a source of As (Fendorf, 2010; Kocar et al., 2008; Polizzotto et al., 2008). However, in riparian wetlands, when the water level decreases, consequently to the decrease in the precipitation volumes and increase in evaporation, the redox conditions become progressively oxidative, and the fate and behavior of As(III) can be questioned. Two possible mechanisms may occur: either As remains bound to OM via thiol groups or metallic bridges or is bound to the newly formed particulate or colloidal Fe(III) minerals. Its oxidation state must be questioned as well; As(III) could be completely or only partially oxidized as As(V). However, few studies have been performed on oxidation products derived from the wetland soil solution to understand their impact on the

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As speciation. ThomasArrigo et al. (2014) investigated oxidation products from a peatland surface solution. They revealed that As was adsorbed onto poorly crystalline Fe(III)-oxyhydroxides as As(V) and As(III). They linked the presence of As(III) to the reduction of As(V) by freshwater green algae present in the Fe(III)-oxyhydroxides flocs. Peatlands and riparian wetlands have different water regimes. Peatlands are generally permanently flooded (i.e. reducing condition) while riparian wetlands are subjected to seasonal flooding (i.e. alternating redox). These discrepancies are of major importance in terms of the OM qualities (i.e. mostly humate for riparian wetlands versus fulvate for peatlands) and properties, mineral reduction/oxidation rates, element fluxes, etc. Al-Sid-Cheikh et al. (2015) showed that oxidation products from riparian wetlands are Fe- and organic-rich and are able to concentrate high amounts of As. Through the statistical treatment of NanoSIMS images and XANES records, they revealed that the As distribution was correlated to the Fe distribution and they highlighted the presence of hot spots highly enriched in As, OM and S but depleted in Fe. They suggested possible interactions between OM, As and S via OM thiol groups. Because the NanoSIMS analysis only shows colocalizations of the elements, detailed spectroscopic investigations are needed to infer the oxidation state and the local coordination environment of As. Because the amount of OM is high in reoxidation compounds (Al-Sid-Cheikh et al., 2015), it should influence the Fe(III)-oxyhydroxide structure and the As oxidation state and speciation.

The purpose of this study was thus dedicated to identify the fate of As when the riparian wetland became oxidized, namely to identify the distribution of the As speciation in oxidation compounds from a naturally poorly As-enriched riparian wetland (Naizin-Kervidy, France). In-situ scavenging devices were used to collect the oxidation products subsequent to the water level decrease in the wetland soil (Al-Sid-Cheikh et al., 2015; Belzile et al., 1989). The bulk and microscale distribution and speciation of As and Fe were investigated by coupling NanoSIMS to XAS experiments ( $\mu$ XANES and  $\mu$ EXAFS).

## 2. Experimental method

### 2.1. Field site description and sample collection

Natural samples were recovered from the Mercy riparian wetland of Kervidy-Naizin located in Brittany in western France at 48°00'42.4" N and – 2°50'20.2" E (decimal degrees). This sub-catchment has been monitored since 1991 to investigate the effects of intensive agriculture (corn culture and livestock) on water quality. The hydrological, pedological and geochemical contexts are therefore well documented (Bourrié et al., 1999; Dia et al., 2000; Gruau et al., 2004; Olivié-Lauquet et al., 2001). The maritime temperate climate is characterized by an annual temperature and precipitation of 10.7 °C and 814 mm days<sup>-1</sup>, respectively. The adjacent stream is ephemeral and does not often flow from the end of August to October. The upper soil horizon was defined as the organo-mineral horizon (Ah) of a planosol (according to the WRB international classification) which contained (wt%; anhydrous basis) OM (15%), clay (42%), quartz (30%) and Fe(III)-oxyhydroxides (3.5%) (Grybos et al., 2007). The samples were collected using the method described in Al-Sid-Cheikh et al. (2015) with a collecting device inspired from Belzile et al. (1989). Polytetrafluoroethylene (PTFE) sheets (10 × 18 cm, 1.5-mm-thick), wrapped in nylon filters for protection (size pore, 67  $\mu$ m), were inserted into the upper horizon of the wetland soil during the water-saturation period (i.e. when the soil solution was reduced). This material was selected because of its inert characteristic and resistance toward aging (Belzile et al., 1989; Teasdale et al., 1998). Under these reducing conditions, soil Fe(III)-oxyhydroxides were reductively dissolved by autochthonous bacteria in the soil (Dia et al., 2015), which subsequently induced the solubilization of a large amount of Fe(II) and other elements, primarily associated with the Fe(III)-oxyhydroxides, such as metals or metalloids. The increase in pH due to H<sup>+</sup> consumption by

the reductive reactions induced the desorption of a large amount of OM from the mineral surfaces (Grybos et al., 2009). The PTFE sheets were inserted under these reduced conditions. When the water table decreased, the soil was progressively water-desaturated. All of the redox-sensitive elements of the reduced soil solution were potentially oxidized, especially Fe(II) which precipitates in the presence of elevated level of OM to produce Fe(III)-OM solids (Al-Sid-Cheikh et al., 2015; Pédrot et al., 2011a). The PTFE sheets mimicked the hydrophobic soil porosity and the oxidation compounds therefore coated their surface. The sheet scavenger method was validated by Al-Sid-Cheikh et al. (2015), who clearly demonstrated that the coated compounds originated from the soil solution. The precipitates on the PTFE device showed an identical rare earth elements (REE) pattern with the wetland soil solution. The REE are strongly adsorbed on OM and Fe(III)-oxyhydroxides and allow these compounds to be traced in the environment (Davranche et al., 2011; Grybos et al., 2007; Tang and Johannesson, 2003). An identical REE pattern between the reduced soil solution and oxidation products demonstrated that precipitated solids on the PTFE device originated from the oxidation of the reduced soil solution without any selection which would have induced a fractionation of REE and a modification of the REE pattern. Moreover the concentrations of Si and Al (indicating the presence of clays) of the precipitates are low and similar to those in the reduced soil solution (Table 2) confirming that the precipitates originated from the soil solution and not from the soil. In the present study, the sheet scavengers were removed from the soil after five hydrological cycles (i.e. five years) which allows us to study the result of all processes occurring during oxidation/reduction cycles in the wetland. Processes including precipitation of diagenetic solids, As adsorption and Fe(III)-oxyhydroxide maturation occurring within the wetland soil are integrated by the sampling method used in this study.

### 2.2. Chemical analyses

The collected soil samples were dried at 30 °C for 72 h, and then sieved to 2 mm. The samples were digested by alkaline fusion using lithium metaborate (LiBO<sub>2</sub>) flux and analyzed for major and trace elements at the SARM facility (Service d'Analyse des Roches et des Minéraux, Nancy, France). Dissolved organic carbon (DOC) concentrations were measured using an organic carbon analyzer (Shimadzu TOC-V CSH). The accuracy of the DOC measurements was estimated to be at  $\pm 5\%$  by using a standard solution of potassium hydrogen phthalate. The iron and As concentrations were determined by ICP-MS using an Agilent technologies 7700  $\times$  at the University of Rennes 1. The samples were pre-digested twice with 14.6 N HNO<sub>3</sub> at 90 °C, evaporated to complete dryness and then resolubilized with HNO<sub>3</sub> at 0.37 mol L<sup>-1</sup> to avoid any interference with the DOC during the analysis. A flux of He was injected in a collision cell to remove interferences from <sup>40</sup>Ar<sup>35</sup>Cl/<sup>75</sup>As and <sup>40</sup>Ar<sup>16</sup>O/<sup>56</sup>Fe. Quantitative analyses were performed using a conventional external calibration procedure (seven external standard multi-element solutions, Inorganic Venture, USA). Rhodium-rhenium was added on-line as an internal standard at a concentration level of 300 mg L<sup>-1</sup> to correct for instrumental drift and possible matrix effects. Calibration curves were calculated from the intensity ratios of the internal standard and the analyzed elements. The international geostandard SLRS-4 was used to control the accuracy and reproducibility of the measurement procedure. The instrumental error on the As and Fe analysis was below 3%. The chemical As and Fe blanks were lower than the detection limits (respectively 0.003 and 0.07  $\mu$ g L<sup>-1</sup>) and were thus negligible.

### 2.3. NanoSIMS sample preparation and data acquisition

Adhesive carbon tapes were used to recover the coated solid layer from the sheet scavengers. The carbon tapes were analyzed without any other NanoSIMS preparation. Measurements were performed

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