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Unravelling the fate of arsenic during re-oxidation of reduced wetland waters: Experimental constraints and environmental consequences

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ABSTRACT

The presence of arsenic(As)-bearing Fe(III) oxyhydroxides in wetland zones may threaten water quality due to the reduction processes that affect these zones. These processes have indeed the potential of releasing As into the soil solutions, and ultimately into the nearby river network, being given the hydrological connectivity that exists between wetlands and rivers. The effective transport of the released As into the river network is however dependent on the behaviour of As during the re-oxidation process that will occur at the wetland–river boundary, which could immobilize the released As into neo-formed Fe(III) oxyhydroxides. One of the key questions is, however, which is the impact of the organic-rich nature of wetland waters on this neoformation, which could instead favour the development of highly mobile As-bearing, organomineral colloids. In this study, we evaluated this possibility by carrying out oxidation experiments on humic acid (HA)- and As(III)/Fe(II)-rich waters. The ultrafiltration results showed that the presence of organic molecules during Fe oxidation events played a major role in the hydrolysis reaction of Fe oxyhydroxides. When Fe microparticles were formed in the absence of HA, the occurrence of HA during Fe oxidation events promoted the formation of amorphous nanosize Fe phase diffusely embedded within the organic matrix. These mixed Fe–HA colloids constrained the fate and distribution of As. These results were confirmed by nanoSIMS images that showed As sorption onto and within Fe microparticles ($> 0.2 \mu\text{m}$) in the absence of HA. By contrast, with HA, results showed preferential incorporation of As in the bulk of Fe–HA colloids ($< 0.2 \mu\text{m}$) during their formation rather than surface adsorption onto these colloids.

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1. Introduction

Arsenic (As) is a toxic element that can lead to wide-scale poisoning in populations when present in waters (Anawar et al., 2003; Fendorf et al., 2010; Smedley and Kinniburgh, 2002). Since wetlands can be an important

source of waters for both ground and river waters, they can transfer As to these hydrosystems for two reasons. Firstly, wetlands can be enriched in As-bearing Fe(III) oxides through erosion and deposition during high-flow periods of flooding (Kocar et al., 2008; Polizzotto et al., 2005). Secondly, the anaerobic conditions that periodically develop in these systems can lead to the reduction of the Fe(III) oxides and to As release within wetland waters, these latter being then able to pollute the water masses with which the wetlands are connected, namely the

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underlying groundwater and the adjacent river network (Anawar et al., 2003; Baeyens et al., 2007; Kalbitz and Wennrich, 1998).

In wetlands categorized as riparian zones (associated with streams), flows out of wetlands are preferentially performed by evapotranspiration, surface runoff, and subsurface water outflow. In these waters undergoing oxidation–reduction events, precipitation or dissolution of carrier phases can play a major role on the mobility of dissolved trace elements. However, the biogeochemistry of the released As is still poorly constrained, particularly as regards to the role played by Fe(II) re-oxidation processes that may occur during the transport of the As from its wetland source to the hydrosystems. Indeed, the re-oxidation process could lead to the precipitation of secondary Fe(III) oxyhydroxide crystals that could immobilize the released As. This process of As scavenging by secondary Fe(III) oxyhydroxides could be a very efficient, naturally occurring attenuation process, particularly in oxygenated hydrosystems, such as streams and rivers. However, this attenuation role of secondary Fe(III) precipitation regards to As transport to streams and rivers could be challenged by the high dissolved organic matter (DOM) concentration of wetland waters that could stabilize the As in solution or lead to the formation of highly mobile Fe(III)-DOM colloids. In fact, several studies already showed that DOM could critically affect the aquatic geochemistry and the fate of As (Fendorf et al., 2010). The formation of As-DOM complexes has been already documented for various As species and DOM types, as well as for various physicochemical environmental media (Buschmann et al., 2006; Liu and Cai, 2010; Liu et al., 2011). The extent of As-DOM binding varies with DOM origin and metal loading (mostly Fe) of the DOM phase (Liu et al., 2011; Redman et al., 2002). Likewise, studies using ultrafiltration techniques have already demonstrated that most of the Fe occurring in wetlands or organic-rich solutions was found in the suspended colloidal fractions (Allard et al., 2004; Gaffney et al., 2008; Pédrot et al., 2008). These colloids may include large DOM species coagulated by chelated Fe and/or stabilized by ferric nano-oxyhydroxides (Pédrot et al., 2011; Pokrovsky et al., 2005). Several authors have recently shown that such Fe-DOM associations could be the carrier phases of As(V) in organic-rich and wetland solutions (Mikutta and Kretzschmar, 2011; Ritter et al., 2006). Arsenic may be either associated with Fe-OM colloids via Fe(III)-cationic bridging or via adsorption/incorporation in Fe(III) solid phases, or directly bound to OM molecules via functional groups, such as -SH (Gorny et al., 2015; Liu and Cai, 2010; Liu et al., 2011; Mikutta and Kretzschmar, 2011).

The occurrence of mixed Fe nano-oxyhydroxides-OM colloids has been assumed in several studies that focused on organic-rich waters (Pédrot et al., 2008; Pokrovsky et al., 2005; Rose et al., 1998). Recent studies dedicated to investigating the ability of DOM to control Fe speciation have demonstrated that Fe(II) oxidation in the presence of organic molecules can promote the formation of small amorphous Fe nano-oxyhydroxides colloids instead of Fe microparticles as DOM inhibits the development of large hydroxide crystals (Gaffney et al., 2008; Pédrot et al.,

2011). The high sorption capacity of these neo-formed Fe nanoparticles makes them important potential transport vectors for contaminants in the environment (Warren and Haack, 2001). Their small size, due to their intimate association with DOM, confers them the capacity of also transporting the contaminants over long distances.

Despite the evidence of environmental occurrences of As-Fe-OM associations, no study has so far investigated in details the behaviour of As during the oxidation of Fe(II) and DOM-rich solutions, despite the potential environmental importance of those associations as potential carriers of As contamination in rivers fed by wetland waters. This study was dedicated to the reporting of a series of experiments, which were conducted to fill this gap. More specifically, oxidation of Fe(II) solutions were carried out with and without the addition of dissolved As and DOM (as humic acid) in order to specify the impact of DOM on the fate of As during Fe(II) oxidation. This was done by combining ultrafiltration experiments and NanoSIMS images. NanoSIMS – Nanoscale Secondary Ion Mass Spectrometers – are ion probes that can be used to obtain precise, spatially explicit, maps of elemental and isotopic distribution in complex matrices with a nanoscale spatial resolution (Herrmann et al., 2007). This technique offers many exciting opportunities for potential applications within the field of biogeochemistry (Herrmann et al., 2007; Moore et al., 2012), and this study may also be viewed as an experimental investigation of the ability of NanoSIMS instruments to map the distribution of As in both pure Fe and mixed Fe-OM colloids.

2. Materials and methods

Three types of Fe²⁺ oxidation experiments were carried out, namely (i) without humic acid (HA) and As, (ii) with As only and (iii) with HA and As. Humic acid suspension was obtained from standard humic acid (Leonardite, 1S104H, IHSS).

An acidified (HCl) 702 mg·L⁻¹ Fe(II) stock solution was prepared with FeCl₂. This solution was then added at 0.1 mL·min⁻¹ with an automated burette (Titrino 794, Metrohm) in a thermostatic beaker set at 25 °C to three suspensions in equilibrium at pH 6.5, namely (i) a 0.01 M electrolyte (NaCl) solution for the Fe system (Exp. 1), (ii) a 0.01 M electrolyte (NaCl) solution containing As(III) for the Fe-As system (Exp. 2), and (iii) a 0.01 M electrolyte (NaCl) solution containing both As(III) and HA for the Fe-As-HA system (Exp. 3). These three suspensions, in contact with the atmosphere, were continuously stirred throughout the Fe(II) oxidation experiments. The buffering capacity of HA in equilibrium at pH 6.5 was tested in Exp. 3 to evaluate the hydroxyl consumption with no change in the pH. Simultaneously in these three suspensions, the pH was continuously maintained at 6.5 by progressively adding 0.1 M NaOH using a second automated burette programmed in a pH stat mode (Titrino 794, Metrohm). The accuracy of the pH measurement was ± 0.04 pH units. At the end of the Fe(II) addition (*t* = 250 min), the suspensions were left in contact with the atmosphere at pH 6.5 for another 750 min. Table 1 shows the Fe_{tot}, As_{tot}, and DOC_{tot} concentrations of suspensions at the end of Fe(II) addition

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