



Highlighting the wide variability in arsenic speciation in wetlands: A new insight into the control of the behavior of arsenic

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Abstract

Although the behavior of Arsenic (As) under reducing conditions in periods of high water levels in wetlands is well understood and documented, there is a lack of information under oxidizing conditions when the water level decreases. In this study, we were interested in the first stage of the oxidizing period, when oxidation products are still in suspension. A soil sample from the Naizin Kervidy wetland (France) was incubated in the laboratory to produce a reduced soil solution. The reduced solution was subsequently oxidized, filtered and ultrafiltered using decreasing pore size membranes (5 μm , 3 μm , 0.2 μm , 30 kDa and 5 kDa). The distribution of As and Fe was investigated in each size fraction of the oxidized solution and their speciations were studied using XAS, HPLC and SEC-ICP-MS. Organic matter was characterized using thermally assisted hydrolysis and methylation gas chromatography–mass spectrometry (THM-GC–MS) and fluorescence spectroscopy. The majority of the As was present as As(V) but a small amount of As(III) still remained despite the advanced oxidized conditions. In the $>0.2 \mu\text{m}$ fractions, the XAS analyses showed that As was associated, in the second shell, with Fe (As–Fe = 3.35 Å) as bidentate binuclear complexes and C (As–C = 2.90 Å), suggesting the integration of As in biological objects. In the $<30 \text{ kDa}$ fraction, As was directly bound to C (As–C = 1.96 Å) in the first shell indicating the presence of organic As species. In the second shell, an As–Fe distance of 3.35 Å was found showing that part of the As was still complexed with Fe. The 0.2 μm –30 kDa fraction was a transitional fraction in terms of the Fe species and OM composition. In this fraction, organic matter exhibited a more humic character (aromatic molecules) inducing an increasing cation binding capacity. As a consequence, in this fraction and in the smallest one, As, Fe and OM seemed to form ternary complexes in which the Fe or nano-oxides in the $>30 \text{ kDa}$ fraction and as monomer, or cluster in $<30 \text{ kDa}$ fraction acted as a bridge. In all of the fractions, a proportion of As(V) was present as organic methylated species. These organic species might be produced by several organisms (animal or plant) via a detoxification process. They seemed to be bound to the particulate and colloidal Fe/OM phases as well as integrated in the remains of the organisms. Mass calculations provided evidence that 90% of the As was contained in the $>5 \mu\text{m}$ particulate fraction and thus was hardly mobile. This study showed that although wetlands have been identified as a potential source of As, a number of biological and geochemical trapping mechanisms also favor As stabilization in wetlands.

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1. INTRODUCTION

Arsenic is a toxic element, and groundwater has been identified as the source of contamination (Smedley and Kinniburgh, 2001). Several mechanisms have been proposed to explain the As contamination of aquifers. Among them, riparian wetlands and floodplains appeared to play a potential role in the As solubilization process (Kocar et al., 2008; Fendorf, 2010). Arsenic enrichment has been identified in many wetland soils (e.g. Anawar et al., 2003; Du Laing et al., 2009). Riparian wetlands and floodplains are organic matter (OM)-enriched zones, adjacent to streams or rivers and are characterized by seasonal flooding. They receive water from three different sources: (i) groundwater discharge, (ii) subsurface flow and (iii) flow from an adjacent surface-water body (Lewis, 1995). During high water levels subsequent to flooding, anaerobic conditions are established and favor the reductive dissolution of wetland soil Fe(III)-oxyhydroxides and associated elements such as As and OM (Olivié-Lauquet et al., 2001; Grybos et al., 2007, 2009; Davranche et al., 2011; Dia et al., 2015). Following its solubilization, As(V) is reduced to As(III), generally by autochthonous bacteria through detoxification or metabolism processes (Dia et al., 2015). When the water table decreases, the soil solution is reoxidized and newly formed Fe(III)-oxyhydroxides are associated with OM precipitate as colloidal aggregates that are able to trap As (Aström and Corin, 2000; Bauer and Blodau, 2009; Sharma et al., 2011; ThomasArrigo et al., 2014). In these aggregates, colloidal or ionic Fe was shown to act as a bridge between As and OM, thus forming ternary complexes (Ritter et al., 2006; Mikutta and Kretzschmar, 2011). These colloidal aggregates represent a first step in the agglomeration process. The formed solids are expected to settle in the soil porosity following the increase of evapotranspiration and the decrease of the water level. Al-Sid-Cheikh et al. (2015) and Guénet et al. (2016) studied similar agglomerates that were collected directly in a wetland soil matrix (Naizin Kervidy, France). They demonstrated that As was heterogeneously distributed in both Fe-enriched zones and OM-enriched/Fe depleted zones. Al-Sid-Cheikh et al. (2015) used NanoSIMS observations to suggest that As in an OM-enriched/Fe-depleted zone could be associated with OM via thiol (SH) binding sites. However, they showed using X-ray absorption spectroscopy that As was mainly bound to OM via Fe(III)-oxyhydroxides, Fe monomers or small clusters occurring as bridges in the ternary system. As a result, the speciation of As in OM-enriched/Fe-depleted zones is still unknown. However, in order to identify the control exerted by wetlands on As solubilization and dynamics, it is essential to understand and explain all of the processes that are able to solubilize or trap As in this type of environment.

Natural oxidized solids, collected in the wetland soil porosity, result from the agglomeration of colloidal aggregates. Therefore, the objective of the present study was to determine the As speciation in these entities. To make it easier to take samples and quantify the analysis, colloidal aggregates were produced in the laboratory subsequent to anoxic incubations of wetland soil. After the soil solution

was sampled and oxidized, the formed aggregates were size-fractionated using filtration and ultra-filtration. A study of the distribution of As, Fe and OM in each size fraction of the oxidized solution was combined with the investigation of As and Fe speciation and OM characterization using multiple techniques. The OM was characterized using THM-GC-MS and fluorescence spectroscopy in each size fraction where the As and Fe speciation was determined by K-edge X-ray absorption spectroscopy (XAS) analysis. The smallest size fractions were investigated using size exclusion chromatography (SEC) combined with an inductive coupled plasma mass spectrometer (ICP-MS) and high-performance liquid chromatography (HPLC) combined with an ICP-MS.

2. MATERIALS AND METHODS

2.1. Site description and soil sampling

Soil was taken from the Mercy riparian wetland in the Kervidy-Naizin sub-catchment located in Brittany in western France. This sub-catchment has been monitored since 1991 to investigate the effects of intensive agriculture (corn cultures and livestock) on water quality. The hydrological, pedological and geochemical contexts are therefore well documented (Bourrié et al., 1999; Dia et al., 2000; Olivié-Lauquet et al., 2001; Gruau et al., 2004). The sampled uppermost 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 dissolved OM (DOM), Fe(II) and trace metal concentrations in the soil solution were found to increase during flooding periods, from 0.83 to 2.5 mmol L⁻¹ (DOM), from 0 to 0.21 mmol L⁻¹ (Fe(II)) and from 0.01 to 0.025 μmol L⁻¹ (As), respectively (Dia et al., 2000; Grybos et al., 2007).

Approximately 5 kg of soil was collected in March 2015 from the surface layer, sieved at 2 mm and stored in the dark at 4 °C to minimize latent biological activity.

2.2. Production of colloidal aggregates

To reproduce the reducing conditions observed in wetland soils, a soil suspension was prepared under anoxic conditions in a Jacomex anaerobic chamber. The soil suspension was prepared in triplicate following the protocol given in Grybos et al. (2007). Approximately 130 g of the sieved soil was mixed with 1.8 L of a synthetic solution containing 0.48 mmol L⁻¹ of NaNO₃ and NaCl, and 0.1 mmol L⁻¹ of Na₂SO₄. The synthetic solution was adjusted to mimic the anionic composition of the soil solution during autumn (the time period when the water table rises) in the Mercy wetland system. The solution was continuously stirred throughout the duration of the anaerobic experiment. The experiments were performed in triplicate with an anhydrous soil/solution ratio of 1/20 (soil moisture = 44 wt%). The extended reduction was followed by monitoring the increase in the pH, Eh and Fe²⁺ and trace element concentration subsequent to the reductive

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