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The impact of oscillating redox conditions: Arsenic immobilisation in contaminated calcareous floodplain soils

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ABSTRACT

Arsenic contamination of floodplain soils is extensive and additional fresh arsenic inputs to the pedosphere from human activities are ongoing.

We investigate the cumulative effects of repetitive soil redox cycles, which occur naturally during flooding and draining, on a calcareous fluvisol, the native microbial community and arsenic mobility following a simulated contamination event.

We show through bioreactor experiments, spectroscopic techniques and modelling that repetitive redox cycling can decrease arsenic mobility during reducing conditions by up to 45%. Phylogenetic and functional analyses of the microbial community indicate that iron cycling is a key driver of observed changes to solution chemistry. We discuss probable mechanisms responsible for the arsenic immobilisation observed in-situ. The proposed mechanisms include, decreased heterotrophic iron reduction due to the depletion of labile particulate organic matter (POM), increases to the proportion of co-precipitated vs. aqueous or sorbed arsenic with α-FeOOH/$Fe(OH)_3$ and potential precipitation of amorphous ferric arsenate.

1. Introduction

Arsenic is an infamous carcinogen (WHO IARC, 2004), ubiquitous in the environment and subject to a variety of mobility altering processes induced by redox changes which occur in temporally flooded soils. The toxicity and mobility of arsenic are dependent on oxidation state and chemical speciation (Bissen and Frimmel, 2003), therefore understanding the effects of repetitive flooding is essential. This is emphasised by recent work showing that hydrological management can impact arsenic mobility in shallow alluvial aquifers (Benner, 2010; Neumann et al., 2010).

Floodplains are used extensively for agriculture (Verhoeven and Setter, 2010), in Europe 79% of riparian area is intensively cultivated (Tockner and Stanford, 2002) despite frequently hosting elevated concentrations of arsenic (Du Laing et al., 2009a; Overesch et al., 2007). Common sources of arsenic include mine-effluent, pesticides and poultry waste (Smedley and Kinniburgh, 2002), although disperse contamination may be geogenic (Winkel et al., 2008) or due to atmospheric deposition (Couture et al., 2008). Tracing arsenic origin on floodplains is problematic due to its mono-isotopic nature, lack of durable chemical source signatures and diverse watershed land-use. Soils in riparian zones frequently act as sinks for river-borne contaminants due to their fine particle size

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and hence high surface area (Lair et al., 2009) but can also act as contaminant sources due to remobilisation (Roberts et al., 2010). Re-mobilised contaminants threaten human health through accumulation in crops (Meharg and Rahman, 2003) and contamination of shallow alluvial aquifers (Ahmed et al., 2004). The current maximum recommended concentration for As in drinking water is 10 μg/L (WHO IARC, 2004) which may be exceeded by remobilisation from sediments (Smedley and Kinniburgh, 2002).

Significant attention has been paid to mechanisms responsible for arsenic mobility in soils during reducing conditions (Islam et al., 2004; McGeehan and Naylor, 1994) and to hydrological transport processes determining arsenic fluxes from sediments (Mukherjee et al., 2008; Nath et al., 2009). Additionally recent field studies have advanced our understanding of the combined hydrological and biogeochemical processes affecting arsenic mobility in nature (Du Laing et al., 2009a; Neumann et al., 2010). However, there is a scarcity of experimental studies accurately isolating biogeochemical processes during the oscillating redox conditions experienced in floodplains, paddy fields, shallow aquifers and other water fluctuating zones (WFZ) (Kögel-Knabner et al., 2010; Stucki, 2011). Experimental studies until now also focused on acidic soils and have not considered carbonate buffered systems (Frohne et al., 2011; Thompson et al., 2006b). It is unclear as to whether cumulative, inter-cycle changes occur over time due to oscillating redox conditions or whether such conditions result in a system which alternates between oxic and reduced end-points. The objectives of this study are to determine the mechanisms controlling arsenic mobility in a carbonate-buffered soil following arsenic contamination, and to improve our understanding of redox-oscillating environments. To simulate redox cycles experienced by floodplain soils, bioreactor experiments were conducted on the top-horizon (0–15 cm) of an arsenic-doped calcic fluvisol prone to phreatic and fluvial inundation. Changes within the bioreactors were monitored throughout the experiment using an array of biogeochemical tools. The sampling location, flooding modes and extent are illustrated in Fig. 1.

Aqueous chemistry (cations, anions, dissolved organic and inorganic carbon (DOC and DIC)), mineralogy (powder X-ray diffraction (XRD)), solid arsenic and iron speciation (X-ray absorption spectroscopy (XAS) and ^{57}Fe Mössbauer spectrometry) were monitored in addition to changes in the bacterial community (16S rRNA). Thermodynamic and kinetic geochemical modelling implemented in PHREEQC (Parkhurst et al., 1999) aided interpretation. The model is used as a diagnostic tool to interpret the measured temporal changes and as a prognostic tool to determine the feasibility of potential mechanisms controlling observed changes in As mobility.

2. Materials and methods

2.1. Field site characterisation

2.1.1. Soil sampling

The soil used in this study was sampled from the eastern floodplain of the Saône River between Macon and Pont-de-Vaux in Ain, France. The land is used for pasture and corn production. Soil was sampled from the top-horizon (0–15 cm) of a mollic-fluvisol in a minor irrigation channel (46.373107°N, 4.879856°E). Established soil sampling protocols were observed (U.S. EPA, 2000).

2.1.2. Soil characterisation

Prior to preliminary and bioreactor experiments the soil was characterised. Elemental composition was determined by total acidic dissolution (HNO_3 + HF + H_2O_2, H_3BO_3 + HF)(U.S. EPA, 1996) and ICP-MS analysis (Agilent 7500ce, Agilent Technologies, France). The particle size distribution was analysed by laser granulometry (Malvern Mastersizer 2000, Malvern instruments, France) and the bulk mineralogy by XRD (full methodology described in 3.5).

2.1.3. Preliminary experiment: determination of natural redox oscillations within the study area

To aid experimental design of bioreactor experiments, the extent of redox fluctuation occurring naturally in the soil during flooding was determined in a preliminary flooding experiment. A passive diffusion pore-water sampler was deployed (Hesslein, 1976) in the soil, within a polycarbonate box which was subsequently flooded for 30 days. This setup has been previously described by Guedron et al. (2011). The pH, Eh, anions, cations and Fe speciation (Stookey, 1970) in resulting pore water were analysed. A description of the sampling device and analyses is provided in the Supplementary Information (Section 1.2.1).

2.2. Main experimental design and redox oscillation procedure

A bioreactor system, based on designs by Thompson et al. (2006b) was filled with 1 L of soil suspension (<1 mm fraction, 100 g L^{-1}) equilibrated for 1 month with 12 mM of arsenic (sodium-arsenate) in order to simulate a severe point source contamination event. The suspension was subjected to multiple cycles of reduction and oxidation to determine the cumulative effects of redox-cycling on arsenic mobility. Eh variation was induced by modulation between sparging of N_2 (7 days) and air (7 days). A total of 5.5, 14 day cycles over a period of 77 days were conducted at constant temperature (30 °C) with sampling on days 1, 4 and 7 of each half-cycle. Each 14 day cycle effectively served a reproducible replicate of the previous cycle and therefore full replicate experiments were not conducted.

2.3. Aqueous chemistry analyses

All chemicals were analytical grade from Fluka, Sigma–Aldrich or Merck. Standards and reagents were prepared with 18 MΩ cm^{-1} water (Millipore). Syringe-sampled soil suspensions were centrifuged and the supernatant filtered to 0.22 μm prior to all aqueous analysis. Analysis of total Na, K, Ca, Mn, Fe and As concentrations in the aqueous phase was performed with ICP-OES after dilution and acidification, using a Perkin Elmer OPTIMA 300 DV (Perkin Elmer, France). Matrix-matched standards were used for all calibrations and NIST validated multi-elemental solutions were used as internal controls. DOC/DIC concentrations were determined using a Shimadzu TOC-5000 (Shimadzu, France), all glassware was burned at 400 °C for 4 h before use. Chloride, Nitrate and Sulphate were analysed by ion chromatography using a Metrohm 761 Compact IC. Eh and pH were recorded every 30 s within the reactors using Xerolyt Solid polymer open-junction electrodes. All aqueous analyses were conducted in triplicate and the error for all techniques was <5%. A more detailed description of the sampling and analytical procedures is provided in Supplementary Information.

2.4. Microbial community analysis

To monitor changes in the composition of the bacterial community during the experiment additional suspension samples were taken on days 7 (reducing), 67 (oxic) and 77 (reducing). Two-gram suspension sub-samples, concentrated by centrifugation, were used for DNA and RNA extractions. Bacterial 16S rRNA sequence libraries were generated from extracted DNA and RNA in order to characterise the microbial community and identify organisms which were metabolically active. The full extraction, amplification and sequencing procedures are described in Supplementary Information (Section 1.3.1). Subsequent phylogenetic analysis was conducted using the ARB software package with the Silva 98 database (Ludwig et al., 2004; Pruesse et al., 2007). Sequences generated have been deposited in the Genbank database (accession numbers: JQ976475-JQ976602) (Fig. 2).

2.5. Powder X-ray diffraction analysis

Powder XRD analysis of mineralogy was conducted on days 1 and 77. Less than 2 mm, 2 μm and 0.2 μm fractions were analysed using a Bruker D5000 equipped with a Kevex Si(Li) solid detector and a Cu $K_{\alpha 1+2}$ radiation source. Larger fractions were wet ground in a centrifugal mill. Intensities were recorded at 25 °C over a range of 2–80° 2θ with a step interval of 0.02° 2θ and a counting time of 3 s per step. Full-widths at half-maximum intensity (fwhm) were determined for diffraction maxima using the EVA program (Bruker).

2.6. ^{57}Fe Mössbauer spectroscopy

Mössbauer spectrometry was performed on solid fractions (obtained by centrifugation) sampled on days 4, 14, 70 and 77. Solids were deposited on polycarbonate holders which were capped and sealed with epoxy resin. Samples were placed in an anoxic container (N_2 atmosphere) before transport for Mössbauer analysis to a cryostat where the sample was maintained under He atmosphere.

The Mössbauer spectra were recorded at 77 K using a constant acceleration spectrometer and a ^{57}Co source diffused into a rhodium matrix. Velocity calibrations were conducted using α-Fe foil at room temperature (RT, 295 K). Mössbauer spectra were described using the Mosfit model (MOSFIT: Teillet and Varret unpublished program) using a combination quadrupolar doublets and magnetic sextets. The height, shift and hyperfine field parameters of these components were then compared to reference values in order to determine structural and speciation information (Fig. 5). The proportion of each iron phase may also be determined from the relative sorption area.