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# Biogeochemistry of arsenic in a highly polluted agricultural soil: Influence of water saturation and organic substrate supply

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**ABSTRACT:** Some agricultural soils were historically polluted by the destruction of chemical shells. The present work used laboratory experiments aiming to determine the influence of water saturation and organic substrate supply on the speciation and mobility and speciation of arsenic (As). A column filled with soil was fed with synthetic water, transiently supplied with organic substrates, during 320 days. Important quantities of As were leached. The initial As(V) present in soil was reduced to As(III) during the periods of organic substrates supply. Most of the As initially present in the solid phases was reduced at the end of experiment. Active As-transforming microbes were quantified in the solids and the evolution of their relative concentrations seemed to be linked to As speciation. The proportion of *aioA* genes encoding an arsenite oxidase, expressed as the ratio of *aioA*/16S genes abundances, tended to increase with the proportion of As(V) in the solids. The microbial activities played a major role in the evolution of As speciation, probably influencing As mobility.

## 1 INTRODUCTION

Arsenic (As) is a toxic element whose transfer from soil to agricultural products may induce health issues (Upadhyay *et al.*, 2019). The bio-availability and mobility of As depends on its speciation, itself influenced by the redox conditions that could substantially vary in soils according to water saturation. These conditions limit O<sub>2</sub> diffusion in pore space implying that reductive redox couples become predominant. If these anaerobic conditions are maintained during several days, reduction of oxidized As could occur. These reactions are microbially driven and imply organic substrates as electron donors. The reduced As species are more mobile, promoting their transfer either to plant or groundwater. The influence of anaerobic periods on the biogeochemistry of As needs to be evaluated extensively in agricultural areas affected by As pollution or high As geochemical background. Here, the effect of anaerobic periods on As biogeochemistry was examined applying complementary geochemical and microbiological monitoring methods.

## 2 MATERIALS AND METHODS

### 2.1 Experimental methods

The soil was sampled in an agricultural site polluted by the destruction of As-containing chemical shells near Verdun, France. It contained 983 ppm total As, mainly in the As(V) form. A glass column (30 cm high, 3.5 cm inner diameter, water jacket maintained at 20°C) was filled with polluted soil sieved at 2 mm and up-flow fed with oxygenated synthetic water (Werber 1991) during 320 days. Anaerobic conditions were induced in the column by supplementing the inlet water with organic substrates (acetate 10 mM, lactate 10 mM, formate 10 mM and glucose 2 mM).

### 2.2 Analysis

As speciation in water was determined by AAS after separation of As(III) and As(V) on resins. As speciation in solids was determined by HPLC-ICP-MS after extraction with H<sub>3</sub>PO<sub>4</sub>. MPN of As(III)-oxidizing and As(V)-reducing microbes (Thouin *et al.*, 2019) and quantification of 16S rRNA, *aioA* and *arsB* genes (Fernandez-Rojo *et al.*, 2017; Poirel *et al.*, 2012) were performed on the soil samples at the end of the experiment.

## 3 RESULTS AND DISCUSSION

### 3.1 Evolution of As speciation and concentration in the column outlet

Concentration of As increased from 5 mg/L to 30 mg/L at the beginning of the experiment (Figure 1) and then decreased between day 40 and day 170. After 160 days, As concentration fluctuated slightly around 5 mg/L. At the end of the experiment, 120 mg of As had been leached from the column. Until day 40, As (V) was the dominant As species.

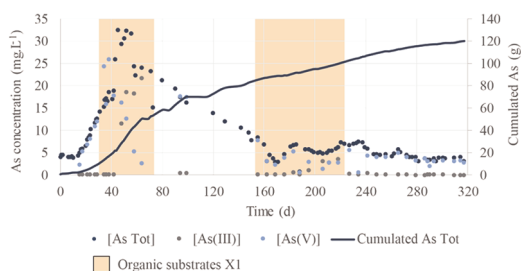


Figure 1. Concentrations of total As, As(III), As(V) and cumulative As in the column outlet water.

With the organic substrate addition, As(V) decreased and As(III) became the main species. During the period with no organic substrate, As(III) in the outlet decreased below 0.5 mg/L.

### 3.2 Final analyses of the solids

As speciation was determined in soil samples of the bottom (outlet) and the top (inlet) of the column at the end of the experiment (Figure 2). As(III) was the main As species in the two samples, and largely preponderant in the bottom zone, whereas As(V) was the main species in the initial soil. As(V) increased from the bottom (60 mg/kg) to the top (174 mg/kg). As(III) also increased but to a lesser extent (from 165 mg/kg to 204 mg/kg).

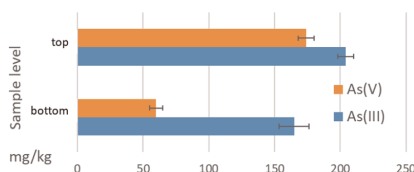


Figure 2. Distribution of As species in the soil at the end of experiment.

The range of numbers of As(III)-oxidizing microorganisms was around  $10^5$ /g of dry soil except at the top of the column (Figure 3). The number of As(V)-reducing microorganisms was the highest in the bottom of the column with about  $10^6$  microorganism per gram of dry soil and then decreased toward the top of the column. The predominance of As(V)-reducing microbes in the bottom of the column might have contributed to the strong reduction of As(V) in the solid phases, resulting in 75% of As(III) in the solids sampled in this zone.

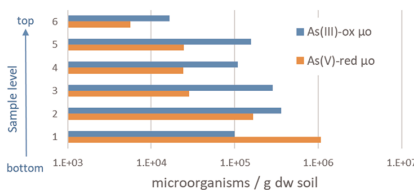


Figure 3. MPN of As(III) oxidizing and As(V) reducing microorganisms in the solids from the column at the end of experiment.

The abundance of *aioA* and *arsB* genes, respectively involved in As(III) oxidation and As(V) reduction, in the soil at the end of the experiment, is given in Figure 4, as the ratio between the functional genes and the 16S rRNA gene. Bacteria owning functional genes related to As transformation were detected in all samples. The proportion of *aioA* genes involved in As(III) oxidation varied irregularly inside the column, however it tended to increase from the bottom (with less As(V)) to the top (presenting a higher proportion of As(V)). The proportion of *arsB* genes also increased from the bottom to the top, but they were 10 times less abundant than *aioA* genes.

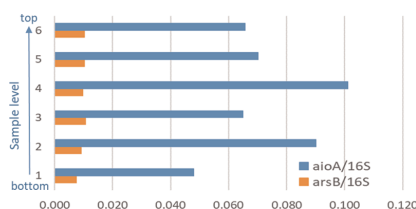


Figure 4. Abundance of genes involved in bacterial As transformation in the soil samples from the column at the end of experiment.

## 4 CONCLUSIONS

Column experiments performed in alternated aerobic and anaerobic conditions showed strong mobility of As and important change of As speciation, both in water and solid phases. An effect of redox conditions on the distribution of As-transforming microbes was also noticed as an original result. These microorganisms could contribute to modifying As speciation so to the distribution of this toxic element between solid and aqueous phases in agricultural soils submitted to transient water saturation events if concentration of electron donor compounds is sufficient.

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