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Influence of environmental changes on the biogeochemistry of arsenic in a soil polluted by the destruction of chemical weapons: A mesocosm study

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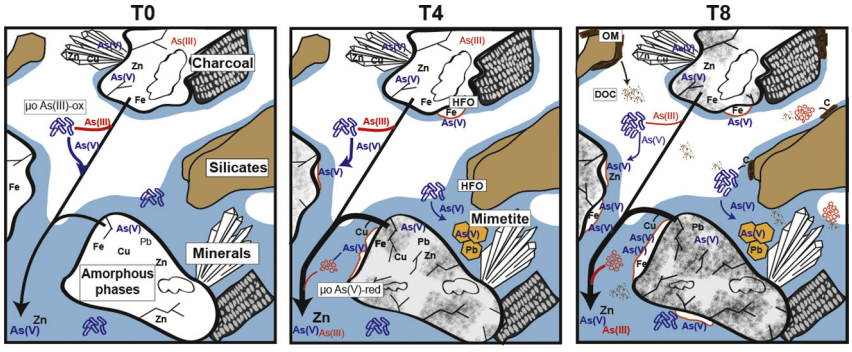
HIGHLIGHTS

- The surface of the main As, Cu and Zn carrier was alterated in water saturated conditions.
- Precipitation of As(V)-bearing mineral mimetite contributed to the immobilization of As and Pb.
- The addition of OM contributed to the growth of As transformation microorganisms.
- As(III)-oxidizing activity was decreased by OM but remained the major As transformation phenomenon in the system.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermal destruction of chemical munitions from World War I led to the formation of a heavily contaminated residue that contains an unexpected mineral association in which a microbial As transformation has been observed. A mesocosm study was conducted to assess the impact of water saturation episodes and input of bioavailable organic matter (OM) on pollutant behavior in relation to biogeochemical parameters. Over a period of about eight (8) months, the contaminated soil was subjected to cycles of dry and wet periods corresponding to water table level variations. After the first four (4) months, fragmented litter from the nearby forest was placed on top of the soil. The mesocosm solid phase was sampled by three rounds of coring: at the beginning of the experiment, after four (4) months (before the addition of OM), and at the end of the experiment. Scanning electron microscopy coupled to energy dispersive X-ray spectroscopy observations showed that an amorphous phase, which was the primary carrier of As, Zn, and Cu, was unstable under water-saturated conditions and released a portion of the contaminants in solution. Precipitation of a lead arsenate chloride mineral, mimetite, in soils within the water saturated level caused the immobilization of As and Pb. Mimetite is a durable trap because of its large stability domain; however, this precipitation was limited by a low Pb concentration inducing that high amounts of As remained in solution. The addition of forest litter modified the quantities and qualities of soil OM. Microbial As

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transformation was affected by the addition of OM, which increased the concentration of both As(III)-oxidizing and As(V)-reducing microorganisms. The addition of OM negatively impacted the As(III) oxidizing rate, however As(III) oxidation was still the dominant reaction in accordance with the formation of arsenate-bearing minerals.

1. Introduction

At the end of the First World War (1914–1918), the former combatants had large stockpiles of unfired munitions. These unspent weapons were dismantled to recycle reusable material, then destroyed or abandoned by ocean dumping or land burial. Chemical weapons containing nitroaromatic, chlorine, bromine or arsenical compounds were destroyed primarily by burning because of their hazardous nature. The site called "Place-à-Gaz", located northeast of Verdun (France), is one of many sites along the western front line where chemical shells were destroyed. Between 1920 and 1928, approximately 200,000 shells containing organo-arsenic compounds were subjected to simple thermal treatment (Bausinger and Preuβ, 2005; Bausinger et al., 2007). The burnt munitions were primarily "blue cross shells" filled with arsenic-bearing vomiting agents CLARK I (diphenylchloroarsine) and CLARK II (diphenylcyanoarsine).

Thermal treatment resulted in severe As and heavy metal contamination of the upper 10–40 cm of topsoil at the site (Bausinger et al., 2007; Thouin et al., 2016). The surface layer where the inorganic contaminants are concentrated corresponds to the combustion residues of the munitions. This layer, composed of slag, scoria, various munitions elements, and large amounts of ash and charcoal from the firewood used for burning, is black in color (Bausinger et al., 2007; Thouin et al., 2016). The central part of the site was heavily contaminated with As, Zn, Cu, and Pb; concentrations of these elements reached 72,820 $mg \cdot kg^{-1}$, 90,190 $mg \cdot kg^{-1}$, 9113 $mg \cdot kg^{-1}$ and 5777 $mg \cdot kg^{-1}$, respectively (Thouin et al., 2016). Most organo-arsenic agents/compounds were oxidized during combustion, resulting in the release of inorganic arsenic As_2O_3 and As_2O_5 (Bausinger et al., 2007). A previous study by Thouin et al. (2016) showed that As was principally present as the pentavalent form (As(V)) within the solid phases (about 98% of arsenate and 2% of arsenite (As(III))) and that several arsenate minerals (adamite-olivenite series and pharmacosiderite) crystallized as the material cooled. An amorphous phase rich in Fe, Zn, Cu, and As and presenting a vitreous texture was also observed, highlighting the association of this unusual mineral assemblage with thermal treatment.

Microorganisms actively contributing to the metabolism of carbon and arsenic were detected at the site despite low organic matter (OM) bioavailability (Thouin et al., 2016). Microbial activity plays a major role in As speciation in soils (de Mello et al., 2007; Yamamura et al., 2009). For example, in mining environment, microbial As-transforming activity was used in biomining of As-bearing minerals and to clean up post mining contamination (Drewniak and Sklodowska, 2013). Several bacterial mechanisms are responsible for As(III) oxidation or As(V) reduction (Battaglia-Brunet et al., 2002; Bachate et al., 2012; Zobrist et al., 2000; Stolz et al., 2002), thus driving As mobility and bioavailability. Changes in environmental conditions, such as modifications of Eh or pH, are likely to modify these microbial activities. Moreover, the concentration and the composition of soil OM affect a microorganism diversity and biomass (Tiedje et al., 1999) and may impact bacterial As transformation (Bachate et al., 2012; Lescure et al., 2016). The cyclic saturation of soils was shown to induce the mobility and change of speciation of arsenic in relation with bacterial activities. Fe and As reduction and release were observed during flooding of contaminated soil (Weber et al., 2010) or redox oscillations (Couture et al., 2015). As-transforming microbes contribute actively to the transformation of As species in frequently saturated soils such as paddy fields (Xiao et al., 2016). However, up to now, the activity of As(III)-oxidizing and As(V)-reducing microorganisms has not been evaluated in highly polluted environments presenting the particular structure and composition of the weapon burning sites, and submitted to fluctuating water regimes.

The contaminated soil at the 'Place-à-Gaz' site is regularly subjected to partial water saturation during periods of high precipitation and run-off because of the underlying clayey formation. Moreover, the margin of the site near the oak forest is exposed to natural deposition of litter that provides bioavailable OM. These environmental variations are capable of altering the carriers phases of As and affect bacterial As transformation activities, thereby changing As mobility at the site.

With the aim to better understand the cycle of As in this highly polluted material submitted to environmental changes, an eight-month experiment was performed in a 1 m^3 mesocosm filled with contaminated material that was subjected to water saturation episodes and input of bioavailable OM. Monitoring of interstitial water composition at different/various depths in the mesocosm and of leachate (outlet water) provided information on the processes that affect the fate of As and other inorganic contaminants and their transfer towards surrounding environmental compartments (Thouin et al., 2017). After Zn, As was the most mobile inorganic contaminant in the soil water, with concentrations ranging from 20 to 110 μM. The present study was focused on the evolution of the solid compartment: mineral phases and arsenic-associated microbial parameters. The goal of this work was to analyze changes in mineral phases and variations in arsenic-associated microbial parameters to increase our understanding of the As cycle in this highly-polluted material that is undergoing environmental exposure.

2. Materials and methods

2.1. Experiment and soil sampling

Soil was collected at the site named 'Place-à-Gaz' (Spincourt Forest, 20 km from Verdun, France) and characterized by Bausinger et al. (2007) and Thouin et al. (2016). It contains slag, coal ash, and residues from ammunition resulting in high concentrations of Zn, As, Cu, and Pb and high organic content (25.9%).

All soil samples described here come from the instrumented mesocosm experiment presented in Thouin et al. (2017) and shown in Supplementary material (SM1). Water and solute fluxes of polluted soil were monitored for 276 days using the experimental device, which consisted of a closed stainless steel column (1 m in diameter and 120 cm high), filled with 610 kg of homogenized contaminated soil. After three months of stabilization, the soil was subjected to dry/wet cycles (over a period of about eight (8) months) and to the addition of organic forest litter at the top of the surface soil at the midpoint of the experiment (after four (4) months at T4) (Fig. 1.a). The dry period was characterized by a saturation limited to the mesocosm bottom, and by the addition of around 12 L of Mont Roucous mineral water once a week. The wet period was characterized by the elevation of the water level and by the addition of 6 L of water every two days. Rainfall was simulated by a sprinkler system. In order to obtain the data previously presented in Thouin et al. (2017), soil solution was sampled at four sampling levels (H1, H2, H3 and H4; Fig. 1.a) thanks to inert porous probes. H1 and H2 levels were permanently unsaturated, H4 level was permanently saturated and H3 level was not saturated during dry periods but was saturated during wet periods.

Coring was performed in the mesocosm using 5 cm diameter stainless steel pipes, at three steps of the experiment: at the beginning (T0), before the addition of fragmented forest litter at the end of