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Characterization and mobility of arsenic and heavy metals in soils polluted by the destruction of arsenic-containing shells from the Great War

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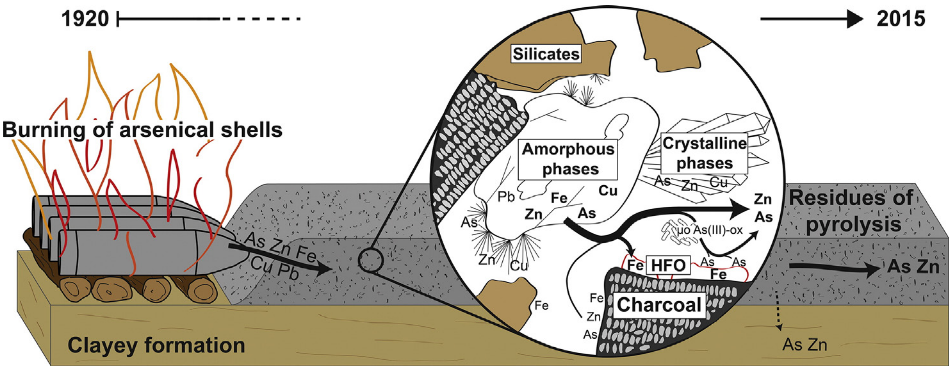
HIGHLIGHTS

- Examination of the complex legacy of chemical shell destruction
- Amorphous phase identified as main As, Cu and Zn carrier
- Unexpected mineralogical association observed
- Potential for bacterial As(III) oxidation detected
- As stability driven mainly by adsorption to hydrous ferric oxides (HFO)

GRAPHICAL ABSTRACT



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ABSTRACT

Destruction of chemical munitions from World War I has caused extensive local top soil contamination by arsenic and heavy metals. The biogeochemical behavior of toxic elements is poorly documented in this type of environment. Four soils were sampled presenting different levels of contamination. The range of As concentrations in the samples was 1937–72,820 mg/kg. Concentrations of Zn, Cu and Pb reached 90,190 mg/kg, 9113 mg/kg and 5777 mg/kg, respectively. The high clay content of the subsoil and large amounts of charcoal from the use of firewood during the burning process constitute an ample reservoir of metals and As-binding materials. However, SEM–EDS observations showed different forms of association for metals and As. In metal-rich grains, several phases were identified: crystalline phases, where arsenate secondary minerals were detected, and an amorphous phase rich in Fe, Zn, Cu, and As. The secondary arsenate minerals, identified by XRD, were adamite and olivenite (zinc and copper arsenates, respectively) and two pharmacosiderites. The amorphous material was the principal carrier of As and metals in the central part of the site. This singular mineral assemblage probably resulted from the heat treatment of arsenic-containing shells. Microbial characterization included total cell counts, respiration, and determination of As(III)-oxidizing activities. Results showed the presence of microorganisms actively contributing to metabolism of carbon and arsenic, even in the most polluted soil, thereby influencing the fate of bioavailable As on the site. However, the mobility of As correlated mainly with the availability of iron sinks.

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1. Introduction

Almost 100 years after the end of the First World War the scars of battle can still be observed along the front line. Hupy and Schaetzl (2008) have studied the effect of shelling on soil structure and landscape recovery after the conflict. The First World War was the first incidence of major warfare that made massive use of chemical weapons. However, very little information is available on the chemical impacts of the conflict on soil, groundwater or wildlife. High concentrations of metals in living organisms and the presence of perchlorate in groundwater along the red zone nevertheless reflect a real impact of this war on the environment (Hube, 2013; Prefectoral decree, Pas de Calais, 25 October 2012).

In the early 2000s, several sites where First World War chemical weapons were destroyed were found to be contaminated by inorganic pollutants. Only two of these were investigated: the first is located in Belgium (Bausinger and Preuβ, 2005) and the second is northeast of Verdun, in France (Bausinger et al., 2007). Chemical shells were disposed of by burning on both of these sites during the 1920s. The munitions destroyed were mainly "blue cross shells" containing organoarsenic warfare agents. The Belgian burning ground has since been used for agriculture (Bausinger and Preuβ, 2005) but the French site, named "Place-à-Gaz", has been unaffected by human activities and undisturbed since destruction of the shells.

Bausinger et al. (2007) showed that the "Place-à-Gaz" had locally limited but severe soil contamination by arsenic, zinc, copper and lead, with concentrations reaching respectively 150 g/kg, 130 g/kg, 15 g/kg and 25 g/kg. The metals came from various parts of the munitions. Shells contained mainly iron, while fuses, driving bands and shell casings were made from copper or zinc. Lead was used for shrapnel balls, primary explosives and chemical warfare equipment. "Blue cross shells" were filled with diphenylchloroarsine (Clark I) and diphenylcyanoarsine (Clark II). These organoarsenic molecules were probably oxidized during the combustion, releasing huge amounts of inorganic arsenic into the surrounding environment. Bausinger et al. (2007) estimated that, over a century, most of the arsenic oxides have been transformed into arsenates or sorbed onto iron oxides or clays, abundant in the inherited soil.

The primary factor influencing mobility of heavy metals in these soils appeared to be pH (Bausinger et al., 2007). Under the site conditions, the soil pH varied from 5 to 6, which favored Cu and Pb fixation in soil, while Zn was more mobile and leached. Arsenic was less affected by pH and behaved differently from metals. However, As concentrations in interstitial waters ($c_{mean} = 838$ μg/L) were significantly higher than the maximum contaminant level (MCL) of arsenic in drinking water as recommended by the World Health Organization (WHO, 1993) in 1993, i.e. 10 μg/L. The mobility of As on the site thus required further investigation.

Arsenic is mainly found in the environment as inorganic species, arsenate As(V) and arsenite As(III) (Cullen and Reimer, 1989). Microbial activities play a major role in As speciation in soil. Different bacterial mechanisms are responsible for As(III) oxidation or As(V) reduction (Santini et al., 2000; Stolz et al., 2002), thus altering As mobility, toxicity and bioavailability (Pierce and Moore, 1982; Masscheleyn et al., 1991). The bacterial activity on former ammunition destruction sites has not been documented to date, but biogeochemistry may explain As speciation and mobility in such environments.

Organic matter, which can have high concentrations in soil (up to 25%), may drive the mobility of metals and arsenic on the site (Bausinger et al., 2007). Indeed, the organic compounds may contain adsorption or complexation sites or induce methylation of metals and metalloids (Saada et al., 2003; Park et al., 2011; Huang et al., 2012). The presence of organic matter also affects bacterial activity. A recent study has shown that As(III)-oxidizing activity in polluted soil can be influenced by the amount of bioavailable organic matter (Lescure et al., in press).

Bausinger et al. (2007) explored the mobility of inorganic pollutants in the "Place-à-Gaz" ground material by sequential extractions. These experiments provided indirect information on the carrier phases but no direct information was available on the mineralogy of soil materials. Moreover, arsenic speciation was not directly determined and no data were available on the activity of microorganisms in this type of heavily polluted soil. Our work focused on the mineralogy, particle size and the geochemistry of the "Place-à-Gaz" surface soils, in order to better understand the behavior of inorganic pollutants on sites polluted by the destruction of chemical weapons. These data were also linked with the mobility of pollutants and biogeochemical parameters.

2. Materials and methods

2.1. Study site

The study site, known as "Place-à-Gaz", is located in the Spincourt forest, 20 km northeast of Verdun, France (Bausinger et al., 2007). At the end of the First World War large amounts of shells and ammunition were stored in the region. In 1920, the Pickett and Fils company was commissioned by the French Ministry of War to destroy these munitions. 200,000 German chemical shells were opened and burned in piles at the center of this area in 1928. The fire was fueled by wood covered with explosive materials.

2.2. Chemical characterization and soil sampling

Total concentrations of As, Cu, Zn and Pb were determined in situ using XL3t800 NITON© portable X-ray fluorescence field apparatus (pXRF), in order to define the metal(loid)s distribution and to target the soil sampling. The signals were calibrated with the chemical analyzes of the soil samples and considered the soil moisture. Maps of As, Cu, Zn and Pb concentrations were drawn by interpolating data by kriging (ArcGIS©).

Four soils were sampled in the surface, non-saturated black layer (0–10 cm) in zones with contrasting vegetation cover. The soils were sieved at 2 mm through sterile sieves, placed in sterile glass jars and stored at 5 °C. Their water content was determined by drying at 105 °C for 24 h. In order to study the chemical composition of different particle size fractions, soil sub-samples were separated into three fractions by mechanical sieve shaker: coarse sand (>200 μm), fine sand (50–200 μm) and loam and clay (<50 μm).

2.3. Soil chemistry and mineralogy

For chemical and mineralogical analyses, the raw soils and particle fractions were ground to 70 μm. Major elements were determined by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) using a Thermo Fischer ICap 6500; trace elements were determined by ICP-mass spectrometry (MS) on a Siex Perkin-Elmer Elan 5000a, both analyses being conducted at the Service d'Analyses des Roches et des Minéraux (SARM — rock and minerals analysis unit of the CRPG-CNRS National Research Institutes). Prior to analysis, the samples were fused with $LiBO_2$ and dissolved in a mixture of 1 N HNO_3, H_2O_2 and glycerol. Organic carbon (C_{org}) and total S were also determined at the SARM center, by carbon and sulfur determination on a Leco SC144 DRPC (SARM, CRPG-CNRS). The mineralogical composition was determined by X-ray diffraction (XRD). XRD patterns were recorded between 0° and 90° (2θ) at a scan rate of 0.3° 2θ cm^{-1} using an INEL CPS120 diffractometer equipped with a Co anode (Co $K\alpha_1 = 1.78897$ Å).

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed to explore the composition and distribution of metals and As in the four soils. SEM was performed on a TM 3000 accompanied by a SwiftED3000 X-Stream module (Hitachi),