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Leaching behavior of arsenic from Upper Cretaceous karst infillings materials in a fractured limestone aquifer (HESP, France)

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ABSTRACT: Arsenic (As) mobility and transport into groundwater are highly dependent on the nature of the sedimentary matrix and the groundwater parameters. In this study, a combination of chemical fractionations, mineralogical characterizations, elemental mappings, and leaching experiments investigated the distribution of As in karst infillings materials from the Hydrogeological Experimental Site of Poitiers (HESP). The influence of pH and Eh conditions, contact time and the presence of bacteria on As mobility were then evaluated. The strong association between iron and As in the matrix is consistent with the low mobility of As in circumneutral pH conditions imposed by the nature of the limestone aquifer. In addition, the alternations of redox conditions tend to increase As release whereas the contribution of the bacteria present in the groundwater seems to regulate the mobilization.

1 INTRODUCTION

Geogenic arsenic (As) contamination in groundwater is a worldwide environmental issue. In this context, it is important to understand the biogeochemical processes involved in the mobilization of As from sedimentary materials into groundwater (Gillispie *et al.*, 2016).

In the present study, the behavior of karst argillaceous infillings materials, with relatively high contents of both organic matter and pyritic minerals, was investigated to understand the mechanisms responsible for retaining As in the Dogger aquifer. This aquifer exhibits high amounts of soluble selenium (Bassil *et al.*, 2016) but no detectable amount of As, in contrast to the associated sedimentary materials, which contain about fourfold higher As than selenium.

For this purpose, the distribution of As was first determined by a combination of elemental mappings and chemical fractionations in the clayey infillings. Then, batch leaching tests were performed to define the impact of pH, redox conditions, and the presence of bacteria on As mobilization.

2 METHODS

2.1 Sampling

The HESP is a research platform that aims to develop new approaches in the characterization

and modeling of groundwater flow and solute transfer. It consists of an area of 10 ha with 37 wells cored through two aquifers: the Middle Jurassic (Dogger) and the infra-Lias aquifers separated by the marls of the supra-Lias. Large paleokarst cavities and smaller modern karst cavities are developed in the Dogger limestone, both partially infilled with dark argillaceous sediments.

Karst infillings samples used in the present study were collected in 2012 through non-destructive drilling at a depth between 66 m and 71 m.

2.2 Laboratory analysis

Chemical quantifications were performed by ICP-MS in an accredited laboratory (CRPG, Nancy, France). Powder samples (infra 50 µm fraction) were analyzed by X-ray diffraction using Phillips analytical X'Pert Pro apparatus in the same experimental conditions as described by Bassil *et al.* (2016). Standard thin sections were observed using a scanning electron microscope Jeol JSM-7900F equipped with a Bruker EDX spectrometer for chemical microanalyses (IC2MP, Poitiers).

A previously developed six-steps protocol of sequential extractions (Mhanna *et al.*, 2019), was used to define the distribution of As, Se, and Fe.

Batch leaching experiments were performed at 20°C in borosilicate flasks with suspensions of 30 g/L. The anaerobic condition was imposed by the addition of a mixture of gases. In situ water

was collected from a HESP well containing no detectable soluble As.

The quantifications of As and Se were performed by ICP-MS (Agilent 7500ce, IPREM, France), and Fe by ICP-OES (Agilent Tech 5110, IC2MP, France).

3 RESULTS AND DISCUSSION

Given the chemical and mineralogical composition of the sample (Table 1), investigations were primarily focused on the distribution of As, selenium, and iron.

Table 1. Main composition of the studied material.

Sample	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	FeO %	Corg %	S tot %	As ppm	Se ppm
C5-Bj	40.6	30.4	1.8	1.1	5.68	0.57	22.4	6.3

Sample	Depth m	Calcite %	Pyrite %	Quartz %	Feld-K %	Anatase %	Clays %	SSA m ² /g
C5-Bj	67.9	4	1.4	9.8	8.1	5.3	71.4	52.2

Petrographic observations identified two pyrite morphologies: euhedral and framboidal, but only the former was rich in As. Around the euhedral crystals, diffuse halos of iron oxide are also enriched in As, but to a lesser extent. Hence, it could be suggested that a part of As coprecipitated or sorbed onto secondary iron oxides, derived from weathering of primary pyrite.

Chemical fractionations supported this assumption since the fractions associated with iron sulfide minerals (35%) and amorphous iron oxides (13%) represented an important part of As (Table 2). The exchangeable fraction was also significant (around 13%) whereas, the soluble As was the least abundant fraction with only 1% of total As.

Table 2. As, Se, and Fe distributions (chemical fractionation).

	As	Se	Fe
Soluble	1.5	4.7	0.2
Exchangeable	13.3	0.7	0.3
Carbonated	8.5	<LD	0.4
Amorphous Fe/Al	13.0	2.2	7.4
Alkaline Soluble	4.8	17.8	1.3
Pyritic	35.4	38.9	82.8
Refractory	23.4	36.3	7.5

Batch leaching studies as a function of pH (Figure 1) showed that As is highly dependent on pH. The negligible leaching in circumneutral pH is consistent with the chemical fractionations and

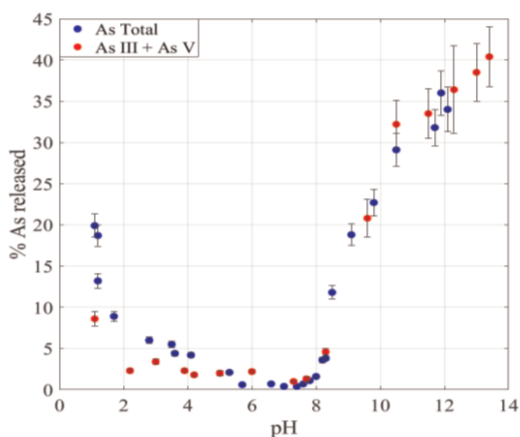


Figure 1. As leaching behavior as a function of pH.

can explain the absence of detectable As in the groundwater of the HESP. The increase of As mobility as pH decreased is attributed to the dissolution of calcite (around pH 4.5), of amorphous iron oxides (around pH 3) and finally of pyritic minerals at very low pH (McKibben *et al.*, 1986).

Leaching experiments as a function of time (Figure 2) showed that the alternation between anaerobic (in grey) and aerobic (in white) conditions favored the mobilization of As. Furthermore, the contribution of the bacteria present in the water tended to limit the release of As during anaerobic conditions. The chemical composition of the water also played a major role in the release of As: the carbonated facies of the HESP water strongly limited the mobilization of As, probably by buffering the pH conditions.

Under alkaline conditions, As mobilization drastically increased with the pH increase as

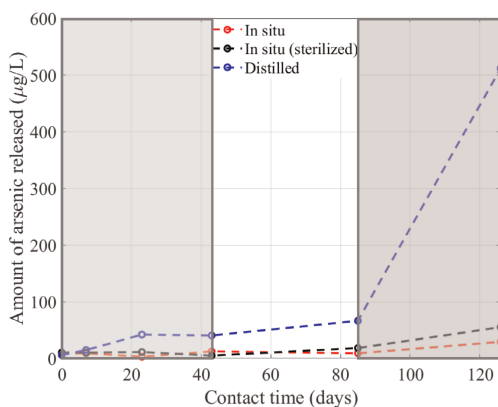


Figure 2. As leaching behavior as a function of time. The grey zone represents anaerobic conditions and the white zone represents aerobic conditions.

previously observed for selenium, iron, and TOC (Bassil *et al.*, 2018), suggesting the presence of ternary complexes between As oxyanions, iron, and humic-like organic matter (Martin *et al.*, 2017).

4 CONCLUSIONS

Elemental mappings combined with chemical fractionations and leaching experiments showed a strong association between As and Fe distributions: After partial alteration of the pyritic materials, the associated As was strongly retained by amorphous iron oxides and continental organic matter complexes. Moreover, the released As was very low in circumneutral pH conditions (as observed in the carbonated aquifer) but highly increased under pH variation. The mobilization of As also increased with the alternations of redox conditions, as observed during the fluctuations of the piezometric levels. Finally, the bacteria seem to play an important role in regulating As mobility under reducing conditions.

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