



Redox behaviour of arsenic in the surface sediments of the Marque River (Northern France)



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ABSTRACT

The behaviour of arsenic(As) in anoxic sediments was studied in the Marque River (Northern France), where concentrations of As are close to the geochemical background level. The distribution of Fe, Mn, S and As species in the solid phase as well as in the pore waters was investigated during four sampling campaigns (February, April, July and October 2014) in order to better understand the parameters involved in the behaviour of arsenic during early diagenetic processes. In the solid phase, As was found to be mainly present in the exchangeable fraction, and the most probable As carrier phases appeared to be amorphous iron, manganese (hydr)-oxides, calcite, and siderite. In pore waters, only the inorganic forms of arsenic [As(III), As(V), and thio-arsenic species] were detected. As(III) was the dominant species, but thio-arsenic species were also evidenced in core depth. No direct interaction between arsenic, iron and manganese cycle has been observed in the pore waters. The behaviour of As is mainly linked to the cycle of sulfur, and especially to the production of sulfides. Overall, this study confirms that the experimental determination of redox speciation is still very useful to understand the behaviour of As during early stages of diagenesis, since application of thermodynamic modelling to redox sensitive environments is not sufficiently constrained yet to provide reliable results.

1. Introduction

Arsenic species are mainly found in the forms of arsenate [As(V)] and arsenite [As(III)] in natural waters and sediments (Gorny et al., 2015a, 2015b, 2015c, and references therein). As the solubility, mobility and toxicity of arsenic depend on its oxidation state (Dixit and Hering, 2003; Jain and Ali, 2000), determination of As speciation and transformation is essential to understand the behaviour of As in anoxic river sediments. Indeed, these environments are highly complex due to numerous biogeochemical reactions. Early diagenetic processes are directly or indirectly linked to the degradation of sedimentary organic matter by bacteria in the first centimeters of the sedimentary column. Mineralization occurs through various metabolic processes, where the organic matter serves as a reducing agent (electron donor). This oxidative process involves the transfer of electrons between oxidants (electron acceptors) from O₂, NO₃⁻, Mn(III, IV) and Fe(III) (hydr)-oxides, and finally SO₄²⁻ (Bernier, 1980). Redox transformations of these major species, combined with other bacterial processes, *i.e.*, methylation, are capable to deeply modify the speciation and the fate of

arsenic within the first centimeters of the sedimentary column, as well as its potential toxicity toward the aquatic organisms (Borch et al., 2009; Gorny et al., 2015a; Páez-Espino et al., 2009).

In the mineral particles, arsenic is usually found in association with aluminum, iron and manganese (hydr)-oxides, carbonates, and sulfide minerals (Drahota et al., 2009; Sadiq, 1995), with various degree of mobility. In particular, sorption processes play an important role on the control of As speciation and mobility (Bowell, 1994; Dixit and Hering, 2003). In the literature, most of the studies that focused on the sorption mechanisms were based on the examination of arsenic fractional distribution (Keon et al., 2001; Wenzel et al., 2001), the identification of As species associated with the exchangeable fraction in the solid phase (Orero Iserte et al., 2004), or the specific interaction between arsenic species and minerals (Wang and Mulligan, 2008). However, the number of experimental studies dedicated to the behaviour of As species with time and depth in pore waters remain scarce (Chaillou et al., 2003; Couture et al., 2010; Deng et al., 2014; Fabian et al., 2003).

This study aims to improve the understanding of As behaviour under the redox constraints induced within surface river sediments that

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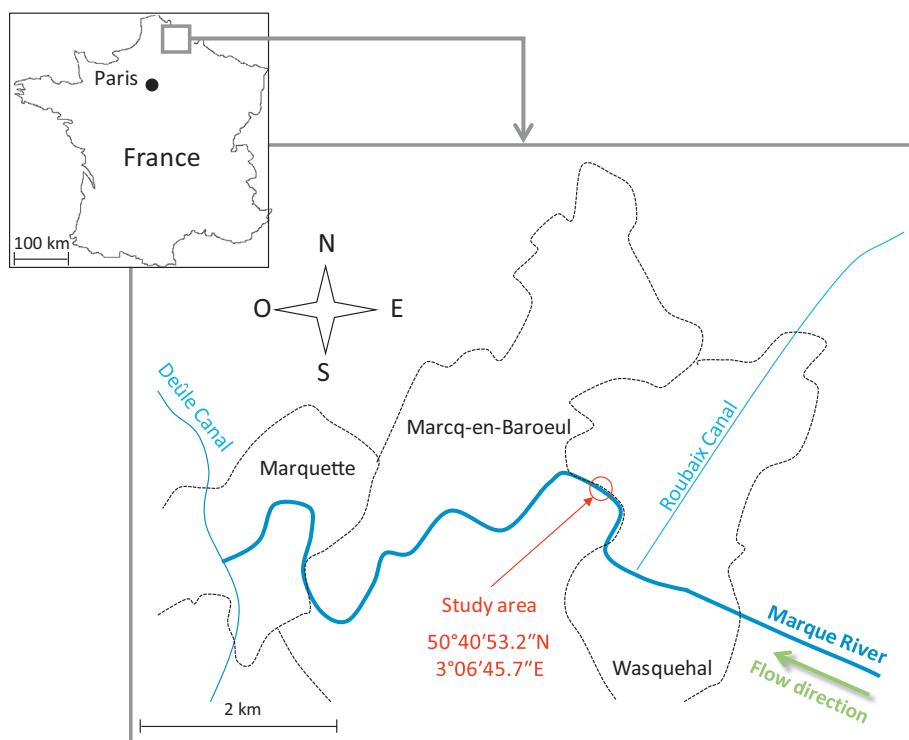


Fig. 1. Localization of the Marque River.

contain large amounts of biodegradable organic matter. For this purpose, the distribution of both As and other key elements (such as Fe, Mn and S) that potentially control the fate of As was studied in the sediment solid phase of the Marque River through sequential extractions. In addition, analyses of pore waters were performed by HPIC-ICP-MS to assess As speciation. The use of redox potential values will also be discussed to demonstrate that thermodynamic equilibrium modelling is inadequate when redox speciation is involved, and to point out the limits of geochemical modelling in such complex environments.

2. Materials and methods

2.1. Location and sampling

The Marque River, located in Northern France, was chosen as the sampling site (Fig. 1). The river rises at Mons-en-Pévèle. The watershed area is about 217 km² with an average slope gradient of 0.1%. The stream runs firstly through a suburban basin (down to Villeneuve d'Ascq), then it goes through an urban basin before it drains to the Deûle River at Marquette-Lez-Lille. The last 7.6 km are channelized but not navigated anymore. The River is characterized by a low flow rate of 1.0 m³ s⁻¹ in average at Forest-sur-Marque, which can reach up to 5.4 m³ s⁻¹ during flood events (Ivanovsky et al., 2016).

Four sampling campaigns were carried out in February, April, July and October 2014 at Marcq-en-Baroeul (Fig. 1) to follow various early diagenesis biogeochemical transformations at different times of the year. Four sediment cores were collected each time using a manual corer equipped with a Perspex® tube (length 35 cm, i.d. 7.5 cm).

The sample processing method is summarized in Fig. 2. The first core was sliced on site every 1–2 cm for the determination of total dissolved As content and As speciation as a function of depth. The cutting operation was done under nitrogen atmosphere in a glove box. The second core was also sliced under nitrogen atmosphere for the determination of alkalinity, Dissolved Organic Carbon (DOC), major elements (Ca, Fe, K, Mg, Mn and Na) and nutrients (NH₄⁺, NO₃⁻, NO₂⁻ and SO₄²⁻) in the pore waters. To do that, each sediment slice was centrifuged with an X 340 Prolabo centrifuge (rotation radius:

20 cm) during 20 min at 2500 rpm in order to extract the pore waters. The samples were subsequently filtered at 0.45 µm (Sartorius syringe filter with cellulose acetate membrane) under nitrogen atmosphere. Prior to the determination of alkalinity, DOC and ions, samples were stored at -18 °C in pre-calcinated (24 h, 450 °C) glass tubes (25 mL with Teflon/silicon septum, Sterilin). Prior to determination of total As, major and minor elements, samples were acidified at 2% (v/v) with HNO₃ (Merck, 65%, suprapur), and stored in polypropylene tubes (PP, 15 mL, Falcon®) at 4 °C. For the determination of As speciation, filtered pore water samples were stored in PP tubes until calibration of HPIC-ICP-MS and determination of As speciation was done (< 3 h). The remaining raw sediments were stored under nitrogen atmosphere at -18 °C for analyses on the solid phase. The analyses in the sediment particles were only performed once time because it has been assumed that the composition of the solid phase has not evolved significantly as the sampling site remained the same and the monitoring was performed within a period of 9 months. For information, the total concentrations, the metal distributions and the reduced sulfur species concentrations have been measured in February, July and October, respectively. The third core was used for the measurement of pH and redox potential every cm within a previously holed Perspex® tube. The fourth core was used for determination of sulfides using AgI-DGT (Diffusive Gradients in Thin films; Teasdale et al., 1999). Surface water was also sampled for analyses following the same procedures, but under oxic conditions and without centrifugation.

2.2. Pore water analyses

Measurements of pH and redox potential were performed using a glass electrode (Mettler Toledo) and a platinum electrode (Mettler Toledo), respectively. Both working electrodes are combined with an Ag/AgCl ([KCl] = 3 M) reference electrode, with a potential equal to 0.22 V versus the Standard Hydrogen Electrode (SHE). All potential values reported in the text are expressed versus the SHE electrode.

Anion concentrations (NO₃⁻, NO₂⁻, SO₄²⁻) were measured using a Dionex™ ion chromatography system equipped with a separation column (IonPacAG18, length 50 mm, i.d. 4 mm, coupled with IonPac

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