

## ARSENIC SPECIATION IN SURFACE SEDIMENTS OF MARQUE RIVER (NORTHERN FRANCE)

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### Introduction

Surface sediments are often recognized for their complexity due to numerous biogeochemical reactions. Early diagenetic transformations are directly or indirectly linked to the degradation of sedimentary organic matter by bacteria. This mineralization occurs through various metabolic processes, where the organic material serves as reducing agent (electron donor). This oxidative process requires transfer of electrons involving oxidants (electron acceptors): O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn(III, IV) and Fe(III) (hydr)-oxides, and finally SO<sub>4</sub><sup>2-</sup> (fermentation processes are not considered in this study). Redox transformations of these major species associated to other bacterial processes (*i.e.*, methylation) are capable to deeply modify the speciation and the fate of arsenic within the first cm of the sedimentary column, as well as its potential toxicity for aquatic organisms.

### Methods

In order to better understand the parameters affecting the speciation and behavior of arsenic in surface sediments, four sampling campaigns were done in 2014 along the Marque river (Northern France) and the sediments cores were treated as follows: (i) on site core cutting under nitrogen atmosphere; (ii) centrifugation of the slices and filtration under nitrogen for pore water analyses; and (iii) sediment particles freezing under nitrogen. Several key parameters are presented as a function of depth: redox potential, pH, arsenic speciation (by HPIC-ICP-MS), Fe(II), Mn(II), S(-II) in sediment pore waters, and Fe, Mn, S and As distribution in the solid phase.

### Results

The results underline that only inorganic forms of arsenic [As(III), As(V), and thio-arsenical species] are detected in pore waters. Overall, As(III) is the dominant species, with As-S associations at the bottom of the cores. No direct interaction between arsenic, iron and manganese cycle has been observed in the pore waters, and the behavior of As should be rather linked to the cycle of sulfur. In the solid phase, As is mainly present in exchangeable fraction. Low associations have been observed between the reactive phases (*e.g.* calcite, (hydr)-oxides, FeS) and the residual fractions (clays, pyritic compounds and organic matter).

### Conclusion

Seasonal changes of As speciation in the dissolved phase depends mainly of S(-II) production by sulfate-reducing bacteria, which makes the amount of dissolved S(-II) an important parameter to follow through time since the As reduction increases its mobility and toxicity.