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# Redox behavior of arsenic in surface sediments of Marque River (Northern France)

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## Abstract

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 organic matter by bacteria. This mineralization occurs through various metabolic processes, where the organic material serves as reducing agent. This oxidative process requires transfer of electrons involving oxidants: 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.

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 and the sediments cores were treated as follows: (i) *on site* core cutting under nitrogen atmosphere; (ii) centrifugation of the slices and (iii) filtration under nitrogen for pore water analyses. Several key parameters are presented as a function of depth: Eh, pH, arsenic speciation (by HPIC-ICP-MS), Fe(II), Mn(II), S(-II) in sediment porewaters, and Fe, Mn, S and As distribution in the solid phase.

The results underline that only inorganic forms of arsenic [As(III), As(V), and thio-arsenical species] are detected in porewaters. 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 cycles has been observed in the porewaters, 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).

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